



1755  
PATENT  
Attorney Docket No. CYC-041

THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT(S): Wang  
SERIAL NO.: 10/040,530 GROUP NO.: 1755  
FILING DATE: January 7, 2002 EXAMINER: Not Yet Assigned  
TITLE: POLYMER-CONTAINING ORGANO-METAL CATALYSTS

RECEIVED  
MAY 15 2002  
TC 1700

**CERTIFICATE OF FIRST CLASS MAILING UNDER 37 C.F.R. 1.8**

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*Sarah Carletti*  
\_\_\_\_\_  
Sarah Carletti

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Submitted herewith is/are:

1. Transmittal Form (1 pg.);
2. Supplemental Information Disclosure Statement (2 pgs.);
3. Form PTO-1449 (1 pg.); with reference (A78-A86; B32-B37; C21-C22)
4. This Certificate of First Class Mailing under 37 C.F.R. 1.8 dated May 9, 2002
5. mailroom postcard



# TRANSMITTAL FORM

Application Serial Number	10/040,530
Filing Date	January 7, 2002
First Named Inventor	Wang
Group Art Unit	1755
Examiner Name	Not Yet Assigned
Attorney Docket No.	CYC-041
Patent No.	Not applicable
Issue Date	Not applicable

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## ENCLOSURES (check all that apply)

<input type="checkbox"/> Fee Transmittal Form <input type="checkbox"/> Check Attached <input type="checkbox"/> Copy of Fee Transmittal Form	<input type="checkbox"/> Copy of Notice to File Missing Parts of Application (PTO-1553) <input type="checkbox"/> Formal Drawing(s)	<input type="checkbox"/> Notice of Appeal to Board of Patent Appeals and Interferences
<input type="checkbox"/> Amendment/Response <input type="checkbox"/> Preliminary <input type="checkbox"/> After Final <input type="checkbox"/> Affidavits/declaration(s) <input type="checkbox"/> Letter to Official Draftsperson including Drawings [Total Sheets ____]	<input type="checkbox"/> Request For Continued Examination (RCE) Transmittal <input type="checkbox"/> Power of Attorney (Revocation of Prior Powers) <input type="checkbox"/> Terminal Disclaimer	<input type="checkbox"/> Appeal Brief (in triplicate) <input type="checkbox"/> Status Inquiry <input checked="" type="checkbox"/> Return Receipt Postcard <input checked="" type="checkbox"/> Certificate of First Class Mailing under 37 C.F.R. 1.8 <input type="checkbox"/> Certificate of Facsimile Transmission under 37 C.F.R. 1.8
<input type="checkbox"/> Petition for Extension of Time	<input type="checkbox"/> Executed Declaration and Power of Attorney for Utility or Design Patent Application	<input type="checkbox"/> Additional Enclosure(s) (please identify below)
<input checked="" type="checkbox"/> Supplemental Information Disclosure Statement <input checked="" type="checkbox"/> Form PTO-1449 <input checked="" type="checkbox"/> Copies of IDS Citations (A78-A86; B32-B37; C21-C22)	<input type="checkbox"/> Small Entity Statement <input type="checkbox"/> CD(s) for large table or computer program	
<input type="checkbox"/> Certified Copy of Priority Document(s)	<input type="checkbox"/> Amendment After Allowance	
<input type="checkbox"/> Sequence Listing submission <input type="checkbox"/> Paper Copy/CD <input type="checkbox"/> Computer Readable Copy <input type="checkbox"/> Statement verifying identity of above	<input type="checkbox"/> Request for Certificate of Correction <input type="checkbox"/> Certificate of Correction (in duplicate)	

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## SIGNATURE BLOCK

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Assistant Commissioner for Patents  
Washington, D.C. 20231

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Sir:

In accordance with the provisions of 37 C.F.R. 1.97 and 1.98, Applicants hereby make of record the patents and publications listed on the accompanying Form PTO-1449, and other information contained herein, for consideration by the Examiner in connection with the examination of the above-identified patent application. Copies of the patents and publications are enclosed.

REMARKS

In accordance with the provisions of 37 C.F.R. 1.97, this statement is being filed (CHECK ONE):

- ☒ (1) within three (3) months of the **filing date** of a national application other than a continued prosecution application under 37 C.F.R. 1.53(d), or within three (3) months of the **date of entry of the national stage** as set forth in 37 C.F.R. 1.491 in an international application, or before the mailing of the **first Office action** on the merits, or before the mailing of a **first Office action** after the filing of a request for continued examination under 37 C.F.R. 1.114; or
- ☐ (2) after the period defined in (1) but before the mailing date of a **final action** or a **notice of allowance** under 37 C.F.R. 1.311, and
- ☐ the requisite Statement is below, **OR**
- ☐ the requisite fee under 37 C.F.R. 1.17(p), namely **\$180.00**, is included herein, or
- ☐ (3) after the mailing date of a **final action** or **notice of allowance** but before the payment of the **issue fee**, **AND**

- ☐ the requisite Statement is below, **AND**
- ☐ the requisite petition fee under 37 C.F.R. 1.17(p), namely **\$180.00** is included herein.

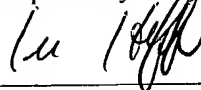
It is respectfully requested that each of the patents and publications listed on the attached Form PTO-1449, and other information contained herein, be made of record in this application.

### STATEMENT

As required under 37 C.F.R. 1.97(e), Applicant(s), through the undersigned, hereby state either that [check the appropriate space only if either (2) or (3) is checked on the previous page and the Statement is required]:

- ☐ 1. Each item of information contained in the Information Disclosure Statement was first cited in any communication from a foreign patent office in a counterpart foreign application **not more than three months** prior to the filing of the Information Disclosure Statement; or
- ☐ 2. No item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing this Statement after making reasonable inquiry, no item of information contained in the Information Disclosure Statement was known to **any individual** designated in 37 C.F.R. 1.56(c) **more than three months** prior to the filing of the Information Disclosure Statement.

Respectfully submitted,



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Reg. No. 41,059

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FORM PTO - 1449

SUPPLEMENTAL INFORMATION DISCLOSURE  
STATEMENT

ATTORNEY DOCKET NO.: CYC-041

APPLICANT(S): Wang

SERIAL NO.: 10/040,530

FILING DATE: January 7, 2002

GROUP: 1755

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## U.S. PATENT DOCUMENTS

EXAM. INIT.		DOCUMENT NUMBER	DATE	NAME	CLASS	SUB CLASS	FILING DATE IF APPROPRIATE
<i>ms</i>	A78	6,369,157 B1	04/09/02	Winckler et al	524	783	03/24/00
	A79	6,376,026 B1	04/23/02	Correll et al.	427	512	12/20/99
	A80	10/102,162		Wang et al			03/20/02
	A81	09/974,722		Phelps et al			10/09/01
	A82	09/945,233		Faler			08/31/01
	A83	09/906,385		Wang			07/16/01
	A84	09/874,706		Wang			06/05/01
	A85	09/754,943		Winckler et al			01/04/01
✓	A86	09/659,975		Phelps			09/12/00

## FOREIGN PATENT DOCUMENTS

EXAM. INIT.		DOCUMENT NUMBER	DATE	COUNTRY CODE	CLASS	SUB CLASS	FILING DATE	ABSTRACT ONLY	ENGLISH LANG Y/N
<i>ms</i>	B32	1,108,921	04/10/1968	GB				No	Yes
	B33	0714926 A2	06/05/1996	EP				No	Yes
	B34	02/22738 A2	03/21/2002	WO				No	Yes
	B35	02/18476 A2	03/07/2002	WO				No	Yes
	B36	01/53379 A1	07/26/2001	WO				No	Yes
✓	B37	99/25485	05/27/1999	WO				No	Yes

## OTHER ART, JOURNAL ARTICLES, ETC.

EXAM. INIT.	OTHER DOCUMENTS: (Including Author, Title, Date, Relevant Pages, Place of Publication)	
<i>ms</i>	C21	Brunelle et al. (1997) "Semi-crystalline Polymers via Ring-Opening Polymerization: Preparation and Polymerization of Alkylene Phthalate Cyclic Oligomers" <i>Polymers Preprints</i> vol. 38, No. 2, pp. 381-382.
<i>ms</i>	C22	Lui et al. (1999) "Preparation of Cyclic Polyester Oligomers and Ultra-Low VOC Polyester Coatings" <i>Polymer Reprints</i> , vol. 40, No. 1, pp. 137-138.
EXAMINER: <i>Shirley L.</i>		DATE CONSIDERED: <i>12/18/03</i>

2382147



## UNITED STATES PATENT AND TRADEMARK OFFICE

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UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. 20231  
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A81

APPLICATION NUMBER	FILING DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO	DRAWINGS	TOT CLAIMS	IND CLAIMS
09/974,722	10/09/2001	1711	1032	CYC-046		29	3

CONFIRMATION NO. 7837

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## UPDATED FILING RECEIPT



\*OC000000007261135\*

Date Mailed: 01/03/2002

Receipt is acknowledged of this nonprovisional Patent Application. It will be considered in its order and you will be notified as to the results of the examination. Be sure to provide the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION when inquiring about this application. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please write to the Office of Initial Patent Examination's Customer Service Center. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections (if appropriate).

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Domestic Priority data as claimed by applicant

## Foreign Applications

If Required, Foreign Filing License Granted 10/31/2001

Projected Publication Date: 04/10/2003

Non-Publication Request: No

Early Publication Request: No

## No Docketing Necessary

KM  
Administrator

1-8-02  
Date

## Reviewed &amp; Approved

VPS  
Resp. Asst

1-9-02  
Date

## Title

Organo-titanate catalysts for preparing pure macrocyclic oligoesters

## Preliminary Class

528

ORGANO-TITANATE CATALYSTS FOR PREPARING  
PURE MACROCYCLIC OLIGOESTERS

Technical Field

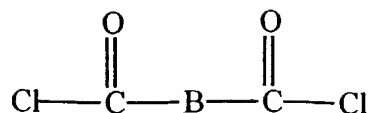
[0001] This invention generally relates to catalysts. More particularly, the invention relates to organo-titanate catalysts useful for preparing macrocyclic oligoesters.

Background Information

[0002] Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss, and solvent resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of techniques including extrusion, compression molding, and injection molding.

[0003] Recently, macrocyclic oligoesters were developed which are precursors to linear polyesters. Macrocyclic oligoesters exhibit low melt viscosity, which can be advantageous in some applications. Furthermore, certain macrocyclic oligoesters melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate catalyst, polymerization and crystallization can occur virtually isothermally.

[0004] One method for synthesis of the macrocyclic oligoesters includes the step of contacting a diol of the formula HO-A-OH with a diacid chloride of the formula:



where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such amines is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is between about -25°C and about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

**[0005]** Macrocyclic oligoesters may also be prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as triethylamine, in a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

**[0006]** Another method for preparing macrocyclic oligoesters is to depolymerize linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to macrocyclic oligoesters by heating a mixture of a linear polyester, an organic solvent, and a trans-esterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

**[0007]** To be useful for the preparation of macrocyclic oligoesters, the organo-titanate catalyst should be soluble in the solvent of the depolymerization reaction, should be in a physical state that allows it to be readily added to the reaction, and should be an active catalyst capable of establishing the desired equilibrium in a reasonable time. Catalysts prepared from tetraisopropyl titanate and two equivalents of butanediol, for example, tend to polymerize and gel from solution. To circumvent this gelation, diethylene glycol was used to substitute part of the butanediol. One technique for preparation of organo-titanate catalysts uses butanediol together with diethylene glycol. See, U.S. Patent No. 5,710,086 to Brunelle *et al.* Catalysts prepared according to this method contain moieties of diethylene glycol, which are later incorporated into

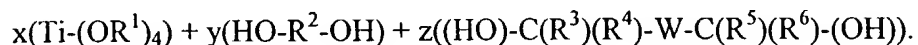
the macrocyclic oligoesters prepared using the catalysts. The incorporation of diethylene glycol moieties causes deleterious effects on the mechanical properties (e.g., modulus) and thermal properties (e.g., melting point and heat distortion temperature) of the polyester prepared from the macrocyclic oligoesters.

[0008] Unfortunately, it is desirable for certain applications such as automotive paint oven or rapid molding and cycle time to employ pure macrocyclic oligoesters, i.e., macrocyclic oligoesters substantially free from macrocyclic co-oligoesters. To conduct molding at high speed, the material (e.g., polybutylene terephthalate polymerized from macrocyclic oligoesters) that is molded needs to crystallize rapidly. High purity is thus required. Also, in making a part by automotive paint oven, the part is less likely to deflect if the material (e.g., polybutylene terephthalate polymerized from macrocyclic oligoesters) has a high heat distortion temperature. In addition, higher crystallinity generally leads to higher modulus and better creep resistance. Furthermore, employing pure macrocyclic oligoesters (e.g., macrocyclic butylene oligoesters) simplifies the manufacturing and product-recovering process as there is no contamination with other diols (e.g., diols derived from diethylene glycol). Methods that lead to pure macrocyclic oligoesters are thus desired.

#### Summary of the Invention

[0009] It has been discovered that organo-titanate catalysts of the invention are useful for preparing macrocyclic oligoesters that are substantially free from macrocyclic co-oligoesters. Further, the organo-titanate catalysts of the invention may be used to prepare macrocyclic co-oligoesters.

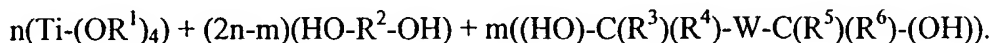
[0010] In one aspect, the invention is directed to a mixture of reaction products of



The mixture is substantially free from di-functional diols other than HO-R<sup>2</sup>-OH. Each R<sup>1</sup> is independently a C<sub>1</sub>-C<sub>10</sub> alkyl group. R<sup>2</sup> is a C<sub>2</sub>-C<sub>6</sub> alkylene group. Each of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> is independently a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group except that at least one of R<sup>3</sup> and R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub> alkyl group and at least one of R<sup>5</sup> and R<sup>6</sup> is a C<sub>1</sub>-C<sub>4</sub> alkyl group. W is an oxygen atom, a

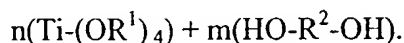
sulfur atom, a nitrogen-containing group, a phosphorus-containing group, or a C<sub>1</sub>-C<sub>4</sub> alkylene group. Each of x and y is greater than 0. In addition, y is larger than z.

[0011] In another aspect, the invention is directed to a mixture of reaction products of



The mixture is substantially free from di-functional diols. Each R<sup>1</sup> is independently a C<sub>1</sub>-C<sub>10</sub> alkyl group. R<sup>2</sup> is a C<sub>2</sub>-C<sub>6</sub> alkylene group. Each of R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> is independently a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group except that at least one of R<sup>3</sup> and R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub> alkyl group and at least one of R<sup>5</sup> and R<sup>6</sup> is a C<sub>1</sub>-C<sub>4</sub> alkyl group. W is an oxygen atom, a sulfur atom, a nitrogen-containing group, a phosphorus-containing group, or a C<sub>1</sub>-C<sub>4</sub> alkylene group. Each of m and n is greater than 0.

[0012] In yet another aspect, the invention is directed to a mixture of reaction products of



Each R<sup>1</sup> is independently a C<sub>1</sub>-C<sub>10</sub> alkyl group. R<sup>2</sup> is a C<sub>2</sub>-C<sub>6</sub> alkylene group. Each of m and n is greater than 0. The ratio of m to n is greater than 2.

[0013] In yet another aspect, the invention is directed to a method for depolymerizing a polyester. The method includes providing one or more of above-described mixtures of reaction products; contacting, in the presence of heat, a mixture including: a polyester, an organic solvent which is substantially free of oxygen and water, and one of the above-described mixtures, to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.

[0014] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following description and claims.

#### Description

[0015] According to the present invention, organo-titanate catalysts are prepared that are useful for catalyzing depolymerization of polyesters to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.

### **Definitions**

[0016] The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

[0017] As used herein, a "macrocyclic" molecule means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

[0018] As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

[0019] As used herein, an "oligoester" means a molecule that contains 2 or more identifiable ester functional repeat units of the same or different formula.

[0020] As used herein, a "macrocyclic oligoester" means a macrocyclic oligomer containing 2 or more identifiable ester functional repeat units of the same or different formula. A macrocyclic oligoester typically refers to multiple molecules of one specific formula having varying ring sizes. However, a macrocyclic oligoester may also include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. A macrocyclic oligoester may be a co-oligoester or multi-oligoester, i.e., an oligoester having two or more different structural repeat units having an ester functionality within one cyclic molecule.

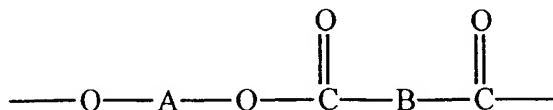
[0021] As used herein, "an alkylene group" means  $-C_nH_{2n}-$ , where  $n \geq 1$ .

[0022] As used herein, "a cycloalkylene group" means a cyclic alkylene group,  $-C_nH_{2n-x}-$ , where x represents the number of H's replaced by cyclization(s).

[0023] As used herein, "a mono- or polyoxyalkylene group" means  $[-(CH_2)_m-O-]_n-(CH_2)_m-$ , wherein m is an integer greater than 1 and n is an integer greater than 0.

[0024] As used herein, a "mixture of reaction products" means a mixture of compounds resulting from a chemical reaction. Thus, a "mixture of reaction products" may refer to a mixture of compounds resulting from a chemical reaction that includes one or more solvents and/or any side products (e.g., a mono- or di-functional alcohol). A "mixture of reaction products" may also refer to a mixture of compounds resulting from a chemical reaction and after removal or separation of one or more solvents or one or more side products, or with the addition of one or more solvents or additives.

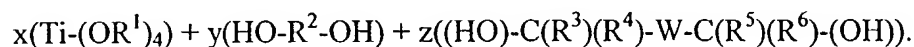
[0025] Macrocyclic oligoesters that may be prepared using the catalysts of this invention include, but are not limited to, poly(alkylene dicarboxylate) macrocyclic oligoesters having a structural repeat unit of the formula:



where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group.

[0026] Illustrative examples of macrocyclic oligoesters include macrocyclic oligoesters of poly(1,4-butylene terephthalate), poly(1,3-propylene terephthalate), poly(1,4-cyclohexylenedimethylene terephthalate), poly(ethylene terephthalate), and poly(1,2-ethylene 2,6-naphthalenedicarboxylate).

[0027] In one aspect, the invention is directed to a mixture of reaction products of



The mixture of reaction products is substantially free from di-functional diols other than  $\text{HO}-\text{R}^2-\text{OH}$ . That is, the mixture is substantially free from  $(\text{HO})-\text{C}(\text{R}^3)(\text{R}^4)-\text{W}-\text{C}(\text{R}^5)(\text{R}^6)-(\text{OH})$ .

"Substantially free" in this context means that the mixture of reaction products is at least 90%, and preferably 95%, free of all di-functional diols other than  $\text{HO}-\text{R}^2-\text{OH}$ , which is determined by the amount of diols originally present.

[0028] Referring to the above formula, each  $\text{R}^1$  is independently a  $\text{C}_1$ - $\text{C}_{10}$  alkyl group, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a pentyl group, or a hexyl group.  $\text{R}^2$  is a  $\text{C}_2$ - $\text{C}_6$  alkylene group, such as an ethylene group, a propylene group, or a butylene group. Each of  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ , and  $\text{R}^6$  is independently a hydrogen atom or a  $\text{C}_1$ - $\text{C}_4$  alkyl group, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group. However, at least one of  $\text{R}^3$  and  $\text{R}^4$  and at least one of  $\text{R}^5$  and  $\text{R}^6$  is a  $\text{C}_1$ - $\text{C}_4$  alkyl group. Thus,  $(\text{HO})-\text{C}(\text{R}^3)(\text{R}^4)-\text{W}-\text{C}(\text{R}^5)(\text{R}^6)-(\text{OH})$  is a secondary or a tertiary alcohol. W is an oxygen atom, a sulfur atom, a nitrogen-containing group (e.g., a  $-\text{N}(\text{R}^7)-$  group, wherein  $\text{R}^7$  is a hydrogen atom or a  $\text{C}_1$ - $\text{C}_8$  alkyl group), a phosphorus-containing group (e.g., a  $-\text{P}(\text{R}^8)-$  group, wherein  $\text{R}^8$  is a hydrogen atom or a  $\text{C}_1$ - $\text{C}_8$  alkyl group), or preferably a  $\text{C}_1$ - $\text{C}_4$  alkylene group such as a methylene



group, an ethylene group, a propylene group, or a butylene group. Each of  $x$  and  $y$  is greater than 0, and  $y$  is greater than  $z$ . Thus, there is more  $\text{HO-R}^2\text{-OH}$  than  $(\text{HO})\text{-C(R}^3\text{)(R}^4\text{)-W-C(R}^5\text{)(R}^6\text{)-}$   
 $(\text{OH})$ .

**[0029]** The reaction of the titanate and the diol(s) may be conducted in an organic solvent or neat. Any organic solvent may be used as long as it does not interfere with the desired reaction and the properties of the mixture of reaction products. Illustrative organic solvents that may be used include, but are not limited to, chlorohydrocarbons such as chloroaromatic hydrocarbons (e.g., *o*-dichlorobenzene). Preferably, no proton donating compounds such as water or acids are present during the reaction.

**[0030]** In one embodiment, the mixture of reaction products is prepared via a metathesis reaction. The reaction may be conducted at any temperature and pressure as long as it yields the desired mixture of reaction products. For example, the reaction may be carried out at a temperature at about 25°C to about 190°C. In one embodiment, the reaction of the titanate and the diol(s) is conducted at about 120°C to about 180°C. In another embodiment, the reaction of the titanate and the diol(s) is conducted at about 140°C to about 170°C. Further, the reaction may be carried out in an inert environment, such as a nitrogen environment, but such conditions are not required.

**[0031]** The reaction is not limited to any particular apparatus or specific processing steps. In one embodiment, the reaction is conducted in a reaction vessel that has stirring/agitation, heating, and distilling/refluxing capabilities.

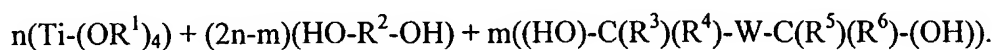
**[0032]** The mixture of reaction products may be used in solution as a depolymerization catalyst. The mixture of reaction products may have a solvent added to it after its formation or the mixture may contain a solvent that was present during the reaction to form the mixture. Additionally the reaction products may be recovered by precipitation from solution with cooling or addition of an anti-solvent, followed by filtration. In addition, volatile components, which may include solvent, may be removed under vacuum, with or without heating.

**[0033]** In one embodiment, each of  $x$ ,  $y$ , and  $z$  is greater than zero and  $y = 2x - z$ . In this embodiment, the molar sum of the starting diols,  $\text{HO-R}^2\text{-OH}$  and  $(\text{HO})\text{-C(R}^3\text{)(R}^4\text{)-W-C(R}^5\text{)(R}^6\text{)-}$   
 $(\text{OH})$ , is twice the molar amount of the titanate,  $\text{Ti-(OR}^1\text{)}_4$ .

[0034] In another embodiment,  $z$  is zero and the ratio of  $y$  to  $x$  (i.e., the molar ratio of  $\text{HO-R}^2\text{-OH}$  to  $\text{Ti-(OR}^1\text{)}_4$ ) is greater than 2, thereby providing excess diol in the reaction starting materials. In this embodiment,  $(\text{HO})\text{-C(R}^3\text{)(R}^4\text{)-W-C(R}^5\text{)(R}^6\text{)-(OH)}$  is not present. In other embodiments, the ratio of  $y$  to  $x$  is greater than 3, greater than 4, or greater than 5.

[0035] In certain embodiments,  $W$  preferably is a  $\text{C}_1\text{-C}_4$  alkylene group, such as a methylene group, an ethylene group, a propylene group, or a butylene group. In other embodiments,  $\text{R}^1$  is an isopropyl group;  $\text{R}^2$  is a butylene group; each of  $\text{R}^3$ ,  $\text{R}^4$ , and  $\text{R}^5$  is a methyl group; and  $\text{R}^6$  is a hydrogen atom. In this embodiment, the titanate is tetraisopropyl titanate, and the diols are 1,4-butanediol and 2-methyl-2,4-pentanediol.

[0036] In another aspect, the invention is directed to a mixture of reaction products of



The mixture of reaction products is substantially free from di-functional diols, such as  $\text{HO-R}^2\text{-OH}$  and  $(\text{HO})\text{-C(R}^3\text{)(R}^4\text{)-W-C(R}^5\text{)(R}^6\text{)-(OH)}$ . Each  $\text{R}^1$  is independently a  $\text{C}_1\text{-C}_{10}$  alkyl group, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a pentyl group, or a hexyl group.  $\text{R}^2$  is a  $\text{C}_2\text{-C}_6$  alkylene group, such as an ethylene group, a propylene group, or a butylene group. Each of  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ , and  $\text{R}^6$  is independently a hydrogen atom or a  $\text{C}_1\text{-C}_4$  alkyl group, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, except that at least one of  $\text{R}^3$  and  $\text{R}^4$  and at least one of  $\text{R}^5$  and  $\text{R}^6$ , is a  $\text{C}_1\text{-C}_4$  alkyl group.  $W$  is an oxygen atom, a sulfur atom, a nitrogen-containing group (e.g., a  $-\text{N(R}^7\text{)-}$  group, wherein  $\text{R}^7$  is a hydrogen atom or a  $\text{C}_1\text{-C}_8$  alkyl group), a phosphorus-containing group (e.g., a  $-\text{P(R}^8\text{)-}$  group, wherein  $\text{R}^8$  is a hydrogen atom or a  $\text{C}_1\text{-C}_8$  alkyl group), or a  $\text{C}_1\text{-C}_4$  alkylene group (e.g., a methylene group, an ethylene group, a propylene group, or a butylene group). Each of  $m$  and  $n$  is greater than 0.

[0037] In this aspect of the invention, the molar sum of the diols,  $\text{HO-R}^2\text{-OH}$  and  $(\text{HO})\text{-C(R}^3\text{)(R}^4\text{)-W-C(R}^5\text{)(R}^6\text{)-(OH)}$ , is twice the molar amount of the titanate,  $\text{Ti-(OR}^1\text{)}_4$ .

[0038] In certain embodiments,  $W$  is a  $\text{C}_1\text{-C}_4$  alkylene group, such as a methylene group, an ethylene group, a propylene group, or a butylene group. In certain embodiments,  $\text{R}^1$  is an isopropyl group. Thus, the titanate is tetraisopropyl titanate. In other embodiments,  $\text{R}^2$  is a butylene group. Thus, one of the diols is 1,4-butanediol.

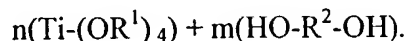
[0039] In yet another embodiment,  $R^1$  is an isopropyl group;  $R^2$  is a butylene group; each of  $R^3$ ,  $R^4$ , and  $R^5$  is a methyl group; and  $R^6$  is a hydrogen atom. In this embodiment, the titanate oxide is tetraisopropyl titanate, and the diols are 1,4-butanediol and 2-methyl-2,4-pentanediol.

[0040] In certain embodiments, the ratio of  $m$  to  $2n$ , which is the molar ratio of starting diol  $(HO)-C(R^3)(R^4)-W-C(R^5)(R^6)-(OH)$  to all starting diols  $(HO)-R^2-OH$  and  $(HO)-C(R^3)(R^4)-W-C(R^5)(R^6)-(OH)$  is within a range from about 0.1 to about 0.5, from about 0.15 to about 0.45, from about 0.15 to about 0.35, or from about 0.15 to about 0.25.

[0041] The mixture of reaction products may further include an organic solvent, which may be added after the reaction. In certain embodiments, the reaction of the titanate and the diols is conducted in an organic solvent. Any organic solvent may be used as long as it does not interfere with the desired properties of the mixture of reaction products. Illustrative organic solvents that may be used include, but are not limited to, chlorohydrocarbons such as chloroaromatic hydrocarbons (e.g., *o*-dichlorobenzene).

[0042] Thus, the mixture of reaction products can be prepared by adding a pre-determined amount of each of  $Ti-(OR^1)_4$ ,  $HO-R^2-OH$ ,  $(HO)-C(R^3)(R^4)-W-C(R^5)(R^6)-(OH)$ , and a solvent if used into a reaction vessel and mixing these reagents at a pre-selected temperature and pressure. Distillation is conducted to remove  $R^2-OH$ . The reaction may be followed by the amount of  $R^1-OH$  (e.g., isopropyl alcohol) liberated from the reaction. Thus, when the reaction is heated to the boiling point of  $R^1-OH$ , the reaction is complete when no more  $R^1-OH$  can be distilled off. Alternatively, the reaction may be monitored using NMR on samples periodically taken from the reaction. Depending on factors including the starting titanate, the starting diols, the ratio of diols and their ratio to the titanate, what solvent is employed, and the reaction temperature and pressure, the mixture of reaction products may take different forms, for example, as a solution, as a solid (i.e., a precipitate from the solution), or as a liquid.

[0043] In yet another aspect, the invention is directed to a mixture of reaction products of



Each  $R^1$  is independently a  $C_1$ - $C_{10}$  alkyl group, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a pentyl group, or a hexyl group.  $R^2$  is a  $C_2$ - $C_6$  alkylene group, such as an ethylene group, a propylene group, or a butylene group. Each of  $m$  and  $n$  is

greater than 0. The ratio of m to n (i.e., the molar ratio of  $\text{HO-R}^2\text{-OH}$  to  $\text{Ti-(OR}^1)_4$ ) is greater than 2.

[0044] In one embodiment,  $\text{R}^1$  is an isopropyl group. Thus, the titanate is tetraisopropyl titanate. In another embodiment,  $\text{R}^2$  is a butylene group. Thus, the diol is 1,4-butanediol. In yet another detailed embodiment,  $\text{R}^1$  is an isopropyl group;  $\text{R}^2$  is a butylene group.

[0045] In certain embodiments, the ratio of m to n, which is the molar ratio of  $\text{Ti-(OR}^1)_4$  to  $\text{HO-R}^2\text{-OH}$ , is within a range from about 2 to about 6. In other embodiments, the ratio is within a range from about 2.5 to about 5.5, from about 3 to about 5, or from about 3.5 to about 4.5.

[0046] Excess  $\text{HO-R}^2\text{-OH}$  may be removed after the reaction, and substantially all of the residual  $\text{HO-R}^2\text{-OH}$  is separated from the rest of the mixture of reaction products. Removal may be effected by conventional techniques such as precipitation, filtration, distillation, and/or vacuum evaporation.

[0047] The reaction between the titanate (i.e.,  $\text{Ti-(OR}^1)_4$ ) and the diol (i.e.,  $\text{HO-R}^2\text{-OH}$ ) may be conducted without a solvent, i.e., neat. Thus, the mixture of reaction products does not include any solvent. However, a solvent may be added to the mixture of reaction products.

[0048] In one embodiment the mixture of reaction products can be prepared by adding a pre-determined amount of each of  $\text{Ti-(OR}^1)_4$  and  $\text{HO-R}^2\text{-OH}$  into a reaction vessel and mixing these reagents at a pre-selected temperature and pressures. Distillation is conducted to remove  $\text{R}^2\text{-OH}$ . The reaction may be followed by the amount of  $\text{R}^1\text{-OH}$  (e.g., isopropyl alcohol) liberated from the reaction. Thus, when the reaction is heated to the boiling point of  $\text{R}^1\text{-OH}$ , the reaction is complete when no more  $\text{R}^1\text{-OH}$  can be distilled off. Alternatively, the reaction may be monitored using NMR on samples periodically taken from the reaction. Depending on factors including the starting titanate, the starting diol, the ratio of diol to the titanate, and the reaction temperature and pressure employed, the mixture of reaction products take different forms, for example, as a solid or a liquid.

[0049] In yet another aspect, the invention is directed to a method for depolymerizing a polyester (e.g., polyester linears). The method includes the step of contacting, in the presence of heat, a mixture containing: a polyester, an organic solvent which is substantially free of oxygen and water, and one or more of the above-described mixtures of reaction products, to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.

[0050] The reaction temperatures that may be chosen in the depolymerization reaction are unlimited. That is, any temperature that results in depolymerization of polyester in the solvent may be employed. However, the depolymerization reaction often is conducted at an elevated temperature. The depolymerization reaction may be conducted below, at, or above the melting point of the polyester to be depolymerized. In one embodiment, the depolymerization reaction temperatures is from about 150°C to about 280°C. In other embodiments, the temperature is from about 180°C to about 260°C, or from about 220°C to about 250°C.

[0051] An organic solvent is typically used in the depolymerization reaction. Any solvent that does not interfere with the depolymerization reaction may be used. Illustrative examples of such solvents include chlorohydrocarbons, such as *o*-dichlorobenzene. The solvent generally is substantially free from oxygen and water. "Substantially free" in this context means a concentration of oxygen less than about 50 ppm, and more preferably less than 10 ppm, and a concentration of water less than about 50 ppm, and more preferably less than 10 ppm.

[0052] There is no limitation with respect to the amount of solvent present in a depolymerization reaction other than the amount results in the dissolution and subsequent depolymerization of the polyester. The concentration of the resulting solution often is less than about 0.5 M. In certain embodiments, the concentration of the resulting solution is less than about 0.3 M, less than about 0.2 M, or less than about 0.1 M.

[0053] The depolymerization reaction is typically conducted under ambient atmospheric pressure and does not need to be conducted in an inert environment. However, the reaction may be conducted in an inert environment, such as a nitrogen or argon environment.

[0054] The amount of catalyst employed in the depolymerization reaction is typically from about 0.5 to about 10.0 mole percent titanate for every polyester monomer unit. In one embodiment, the amount of catalyst employed is from about 1.0 to about 5.0 mole percent for every polyester monomer unit. In another embodiment, the amount of catalyst employed is from about 2.0 to about 3.0 mole percent for every polyester monomer unit.

[0055] There is no limitation with respect to the apparatus or equipment that may be employed to conduct the depolymerization reaction other than allowing the depolymerization of the polyester.

[0056] Polyesters that may be depolymerized to produce macrocyclic oligoesters according to the method of the invention include, but not limited to, poly(alkylene dicarboxylates) such as poly(1,4-butylene terephthalate), poly(ethylene terephthalate), and co-polyesters thereof.

[0057] Macrocyclic oligoesters prepared according to methods of the invention typically are substantially free of macrocyclic co-oligoesters. "Substantially free" in this context means that the weight percentage of macrocyclic co-oligoesters is less than about 10% and preferably less than about 5% of all macrocyclic oligoesters prepared. When the polyester which is depolymerized contains a co-polymer, e.g., poly(1,4-butylene terephthalate) containing poly(ethylene terephthalate), "substantially free" in this context means that the weight percentage of macrocyclic oligoester of butylene, macrocyclic oligoesters of ethylene, and macrocyclic co-oligoester of butylene/ethylene is greater than 90% and preferably greater than 95% of all macrocyclic oligoesters produced.

### Examples

[0058] The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention. The products obtained from these examples may be confirmed by conventional techniques such as proton ( $^1\text{H}$ ) and carbon-13 ( $^{13}\text{C}$ ) nuclear magnetic resonance (NMR) spectroscopy, mass spectroscopy, infrared spectroscopy, differential scanning calorimetry, and gel permeation chromatography analyses.

#### *Example 1*

[0059] A 100 mL flask equipped with a magnetic stir bar and fitted with a septum was flame dried under vacuum then filled with an inert gas. Tetraisopropyl titanate (15 mmol) is added followed by diols (30 mmole) then dry *o*-dichlorobenzene (25 mL). After the addition of all reagents the flask was fitted with a short path distillation head and heated in an oil bath to 140°C for about 1 hour. Isopropyl alcohol liberated from the reaction of tetraisopropyl titanate and the diols was collected and then the solution was heated in 200°C oil to strip off 15 ml of the *o*-dichlorobenzene to ensure that all isopropyl alcohol was removed. Upon cooling the resulting solution was about 1 M in titanium.

*Example 1a Ti- (butanediol: diethylene glycol = 3:1)*

[0060] The preparation is as outlined in Example 1 except that the diol in this case was a mixture of 3 molar parts butanediol and 1 molar part diethylene glycol per molar part of tetraisopropyl titanate. A well-behaved solution (e.g., no gelation) of reaction products resulted.

*Example 1b Ti- (butanediol: diethylene glycol = 1:1)*

[0061] The preparation is as outlined in Example 1 except that the diol in this case was a mixture of 1 molar part butanediol and 1 molar part diethylene glycol per molar part of tetraisopropyl titanate. A well-behaved solution of reaction products resulted.

*Example 1c Ti- (butanediol: diethylene glycol = 0:2)*

[0062] The preparation is as outlined in Example 1 except that the diol in this case was diethylene glycol (2 molar equivalents to tetraisopropyl titanate). Upon cooling the solid titanate precipitated from solution and was collected on a filter and used as a neat solid.

*Example 1d Ti- (butanediol: 2-methyl-2,4-pentandiol = 4:1)*

[0063] The preparation is as outlined in Example 1 except that the diol in this case was 4 mole parts butanediol and 1 mole part 2-methyl-2,4-pentandiol (hexylene glycol) per molar part of tetraisopropyl titanate. The solution was slightly viscous at 1 M. Titanate products gelled from solution above 1.5M.

*Example 1e Ti- (butanediol: 2-methyl-2,4-pentandiol = 0:2)*

[0064] The preparation is as outlined in Example 1 except that the diol in this case was 2 molar parts of 2-methyl-2,4-pentandiol (hexylene glycol) per molar part of tetraisopropyl titanate. A well-behaved thin solution resulted.

*Example 2 Depolymerization*

[0065] Poly(1,4-butylene terephthalate) solutions were prepared at 0.07 M by dissolving poly(1,4-butylene terephthalate) (PBT) in *o*-dichlorobenzene at 180°C under inert atmosphere

(84.8 g of *o*-dichlorobenzene per gram of poly(1,4-butylene terephthalate)). A catalyst was added using a syringe. The reaction was heated at reflux (184°C) until equilibrium was reached (usually within about 1.5 hours). The reaction was sampled and diluted with tetrahydrofuran (5 ml) containing an internal standard (e.g., phenanthrene from Sigma-Aldrich Corp., St. Louis, MO). The sample was then filtered and injected on HPLC gradient program where the individual macrocyclic oligoesters were quantified. Macrocyclic oligoesters isolated from depolymerization reactions were compounded with 0.3 mol% of commercially available butyltin dihydroxide chloride (FASCAT™4101 from Atochem) and polymerized at 190°C for 1 hour. Samples of the resulting polymer are then analyzed by differential scanning calorimetry.

[0066] Results are tabulated below.

**Table 1: Yield and Composition of Depolymerizations**

Experiment	Catalyst	Catalyst level (mol %)	Yield (Macrocyclic Oligoester, % of PBT)	Macrocyclic Co- oligoester (% of Macrocyclic oligoesters)
a	Ti-(BD:DEG=3:1)	4.0	50.3	5.3
b	Ti-(BD:DEG=1:1)	4.0	62.2	11.9
c	Ti-(BD:DEG=0:2)	4.6	82.0	21.1
d	Ti-(BD:HG=4:1)	2.8	51.8	Nd<0.5
e	Ti-(BD:HG=0:2)	3.0	6.9	Nd<0.5

BD: 1,4-butanediol

DEG: diethylene glycol

HG: 2-methyl-2,4-pentandiol (hexylene glycol)

Nd.: Not detected.



**Table 2: Properties of Polymers Prepared from Macrocyclic Oligoesters**

Polymer	Catalyst Preparation, %	Co-monomer (%)	m. p. (T <sub>m</sub> )	Glass Trans. (T <sub>g</sub> )	Crystallinity (%)
PBT	Example 1d, 3%	0	232.2°C	46.8°C	46.4
PBT	Example 1b, 7%	7	223.1°C	44.5°C	39.8
5%PET/PBT	Example 1d, 5%	5	226.0°C	46.1°C	43.3
10%PET/PBT	Example 1d, 5%	10	221.8°C	43.7°C	38.3

PBT: poly(1,4-butylene terephthalate)

PET: poly(ethylene terephthalate)

PET/PBT: co-polyester containing both poly(ethylene terephthalate) and poly(1,4-butylene terephthalate), the percentage being the percentage of ethylene units over the total units of ethylene and butylene.

**Example 3a Ti- (butanediol) 4 eq.**

[0067] A 100 mL round bottom flask equipped with a mechanical stir bar was charged, under argon atmosphere, with butanediol (11.76 g, 130.5 mmol, 4 eq.) and then with tetraisopropyl titanate (9.27 g, 32.6 mmol, 1 eq.). The flask was fitted with a short path distillation head and submerged in a hot oil bath (170°C) to remove isopropyl alcohol from reaction. When the distillation of isopropyl alcohol ceased the flask was cooled to 100°C. Vacuum was applied to strip out any residual isopropyl alcohol. The titanate material was viscous (honey like) at 100°C and became extremely viscous upon cooling to room temperature.

**Example 3b Ti- (butanediol) 3 eq.**

[0068] The procedure of Example 3a was repeated except that the flask was charged with butanediol (12.60 g, 139.8 mmol, 3 eq.) and tetraisopropyl titanate (13.25 g, 46.6 mmol, 1 eq.). This material was extremely viscous even at 120°C, impossible to pump into reactor.

**Example 4 Depolymerization**

[0069] A 250 mL 3-neck flask was equipped with a mechanical stirrer, a short path distillation head, a receiver, and a Claisen head fitted with a thermometer and an inert gas inlet. The flask was charged with *o*-dichlorobenzene (173.8 g), poly(1,4-butylene terephthalate) (1.81 g, plastic

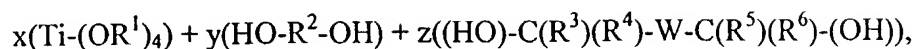
pellets VALOX 315™ from General Electric Plastics Co., Mt. Vernon, Indiana) and was heated in an oil bath to dissolve the plastic pellets. The distillate (22 g) was removed overhead to dry the reactants. Then, a solution of *Ti (butanediol) 4 eq.* in *o*-dichlorobenzene (272 mg as prepared in Example 3a and was dissolved in 3 g of 100°C *o*-dichlorobenzene, 2.8 mol% Titanate) was added. The reaction was held at 180°C and sampled at half hour and at 2 hours to follow equilibration to macrocyclic butylene oligoesters. Yield of macrocyclic butylene oligoesters was 51.5% at half hour and 60.2% at 2 hours. Macrocyclic oligoesters showed no trace of co-oligoester according to HPLC.

[0070] Each of the patent documents disclosed hereinabove is incorporated by reference herein in their entirety. Variations, modifications, and other implementations of what is described herein will occur to those of ordinary skill in the art without departing from the spirit and the scope of the invention as claimed. Accordingly, the invention is to be defined not by the preceding illustrative description but instead by the spirit and scope of the following claims.

# CLAIMS

What is claimed is:

1. A mixture of reaction products of



the mixture being substantially free from di-functional diols other than  $\text{HO}-\text{R}^2-\text{OH}$ ,  
wherein

each  $\text{R}^1$  is independently a  $\text{C}_1\text{-C}_{10}$  alkyl group;

$\text{R}^2$  is a  $\text{C}_2\text{-C}_6$  alkylene group;

each of  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ , and  $\text{R}^6$  is independently a hydrogen atom or a  $\text{C}_1\text{-C}_4$  alkyl group

except that

at least one of  $\text{R}^3$  and  $\text{R}^4$  is a  $\text{C}_1\text{-C}_4$  alkyl group, and

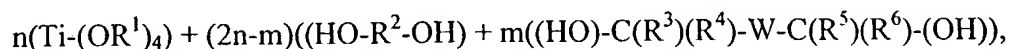
at least one of  $\text{R}^5$  and  $\text{R}^6$  is a  $\text{C}_1\text{-C}_4$  alkyl group;

W is an oxygen atom, a sulfur atom, a nitrogen-containing group, a phosphorus-containing group, or a  $\text{C}_1\text{-C}_4$  alkylene group;

each of x and y is greater than 0; and

$y > z$ .

2. The mixture of claim 1 wherein  $y = 2x - z$  and each of x, y, z is a number greater than 0.
3. The mixture of claim 1 wherein  $z = 0$  and  $y/x > 2$ .
4. The mixture of claim 1 where W is a  $\text{C}_1\text{-C}_4$  alkylene group.
5. The mixture of claim 4 wherein  $\text{R}^1$  is an isopropyl group;  $\text{R}^2$  is a butylene group; each of  $\text{R}^3$ ,  $\text{R}^4$ , and  $\text{R}^5$  is a methyl group; and  $\text{R}^6$  is a hydrogen atom.
6. The mixture of claim 1 wherein the mixture of reaction products is substantially free from all mono- and di-functional alcohols.
7. A mixture of reaction products of

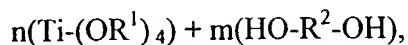


the mixture being substantially free from di-functional diols, wherein

each  $\text{R}^1$  is independently a  $\text{C}_1\text{-C}_{10}$  alkyl group;

$R^2$  is a  $C_2$ - $C_6$  alkylene group;  
each of  $R^3$ ,  $R^4$ ,  $R^5$ , and  $R^6$  is independently a hydrogen atom or a  $C_1$ - $C_4$  alkyl group  
except that  
at least one of  $R^3$  and  $R^4$  is a  $C_1$ - $C_4$  alkyl group, and  
at least one of  $R^5$  and  $R^6$  is a  $C_1$ - $C_4$  alkyl group;  
 $W$  is an oxygen atom, a sulfur atom, a nitrogen-containing group, a phosphorus-containing group, or a  $C_1$ - $C_4$  alkylene group; and  
each of  $m$  and  $n$  is greater than 0.

8. The mixture of claim 7 where  $W$  is a  $C_1$ - $C_4$  alkylene group.
9. The mixture of claim 7 wherein  $R^1$  is an isopropyl group.
10. The mixture of claim 7 wherein  $R^2$  is a butylene group.
11. The mixture of claim 7 wherein  $R^1$  is an isopropyl group;  $R^2$  is a butylene group; each of  $R^3$ ,  $R^4$ , and  $R^5$  is a methyl group;  $R^6$  is a hydrogen atom; and  $W$  is a methylene group.
12. The mixture of claim 7 wherein  $m/2n$  is between about 0.1 to about 0.5.
13. The mixture of claim 12 wherein  $m/2n$  is between about 0.15 to about 0.25.
14. The mixture of claim 7 further comprising an organic solvent.
15. The mixture of claim 7 wherein the mixture is obtained from a reaction conducted in an organic solvent.
16. The mixture of claim 15 wherein the organic solvent is a chlorohydrocarbon.
17. The mixture of claim 16 wherein the organic solvent is *o*-dichlorobenzene.
18. The mixture of claim 7 wherein the mixture of reaction products is substantially free from all mono- and di-functional alcohols.
19. A mixture of reaction products of



wherein

each  $R^1$  is independently a  $C_1$ - $C_{10}$  alkyl group;  
 $R^2$  is a  $C_2$ - $C_6$  alkylene group; and  
each of  $m$  and  $n$  is greater than 0, and  $m/n > 2$ .

20. The mixture of claim 19 wherein  $R^1$  is an isopropyl group.

21. The mixture of claim 19 wherein  $R^2$  is a butylene group.
22. The mixture of claim 19 wherein  $R^1$  is an isopropyl group and  $R^2$  is a butylene group.
23. The mixture of claim 19 wherein  $5 > m/n > 3$ .
24. The mixture of claim 19 wherein the mixture is obtained from a reaction conducted without a solvent.
25. The mixture of claim 19 substantially free of all mono- and di-functional alcohols.
26. A method for depolymerizing a polyester comprising the step of contacting, in the presence of heat, a mixture comprising: a polyester, an organic solvent which is substantially free of oxygen and water, and the mixture of claim 1, to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.
27. The method of claim 26 wherein the polyester comprise poly(1,4-butylene terephthalate).
28. A method for depolymerizing a polyester comprising the step of contacting, in the presence of heat, a mixture comprising: a polyester, an organic solvent which is substantially free of oxygen and water, and the mixture of claim 7, to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.
29. A method for depolymerizing a polyester comprising the step of contacting, in the presence of heat, a mixture comprising: a polyester, an organic solvent which is substantially free of oxygen and water, and the mixture of claim 19, to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.

ORGANO-TITANATE CATALYSTS FOR PREPARING  
PURE MACROCYCLIC OLIGOESTERS

Abstract of the Disclosure

Organo-titanate catalysts are prepared that are useful to catalyze depolymerization of a polyester to produce macrocyclic oligoesters substantially free from macrocyclic co-oligoesters.

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## Title

Methods for converting linear polyesters to macrocyclic oligoester compositions and macrocyclic oligoesters

## Preliminary Class

528

**METHODS FOR CONVERTING LINEAR POLYESTERS TO MACROCYCLIC  
OLIGOESTER COMPOSITIONS AND MACROCYCLIC OLIGOESTERS**

[0001] This application claims priority to provisional patent application U.S. Serial No. 60/229,894 filed on September 1, 2000, the entire contents of which are incorporated by reference herein.

Technical Field

[0002] This invention generally relates to macrocyclic polyesters. More particularly, the invention relates to a method for preparing macrocyclic oligoester compositions from intermediate molecular weight polyesters.

Background Information

[0003] Macrocyclic oligoesters, also called macrocyclic polyester oligomer compositions, can be converted, often under isothermal conditions, to linear polyesters of high crystallinity and solvent resistance.

[0004] One method for preparing macrocyclic oligoesters is accomplished by the reaction of diols, such as ethylene glycol or 1,4-butanediol, with dicarboxylic acid chlorides, such as terephthaloyl chloride or isophthaloyl chloride, under specifically defined conditions. Other methods of preparing macrocyclic polyester oligomer compositions include the reaction of a dicarboxylic acid chloride, such as terephthaloyl chloride, with a bis(hydroxyalkyl) dicarboxylate, such as bis(4-hydroxybutyl) terephthalate.

[0005] Another macrocyclic oligoester preparation method is catalytic depolymerization of linear polyesters such as poly(1,4-butylene terephthalate) ("PBT") and poly(ethylene terephthalate) ("PET"). Catalytic depolymerization macrocyclic oligoester preparation methods require that linear polyesters be purchased or manufactured prior to macrocyclic oligoester production. Producing macrocyclic oligoesters from high molecular weight linear polyesters necessitates handling of a high molecular weight material. The high molecular weight linear polyester material typically has a high viscosity, which requires costly equipment. In some instances it also requires many expensive finishing steps.



[0006] For example, prior art methods employ melt reactors that are capable of generating surface area in high viscosity high molecular weight material. Where poly(butylene terephthalate) is reacted with 1,4-butanediol, it is necessary to generate surface area to enable the diol to diffuse to the surface so that the reaction may proceed to build the molecular weight of the polymer. When high viscosity high molecular weight materials are prepared, diffusion of the diol from the polymer matrix is rate limiting and generating surface area by employing a melt reactor increases the reaction rate of the process of building the molecular weight of the polymer. Such melt reactors are highly engineered, energy intensive, and are run under relatively high vacuum conditions (e.g., 0.5 Torr) that are necessary to handle the high viscosity material.

[0007] Further, U.S. Patent No. 4,590,259 to Kosky et al. describes a method for preparing poly(alkylene terephthalates) of blow molding grade in which a final step is conducted under conditions necessitated by the high melt viscosity of high molecular weight polyesters. A prepolymer preparation step is described in which, for example, a poly(butylene terephthalate) undergoes reaction with 1,4-butanediol. The resulting prepolymer undergoes reaction further with the diol in the presence of an inert gas to reduce the number of acid end groups, for example carboxylic acid end groups, to a desired level. Thereafter, solid state polymerization is conducted whereby the molecular weight of the polymer is increased under high vacuum conditions.

#### Summary of the Invention

[0008] The invention generally relates to methods for depolymerizing linear polyesters to macrocyclic oligomer compositions. In one aspect of the invention, an intermediate molecular weight polyester is employed to prepare a composition comprising a macrocyclic oligoester. In one embodiment, a diol is contacted with a dicarboxylic acid or dicarboxylate in the presence of a catalyst to produce a composition comprising a hydroxyalkyl-terminated polyester oligomer. Thereafter, the hydroxyalkyl-terminated polyester oligomer is heated to produce a composition comprising an intermediate molecular weight polyester which preferably has a molecular weight between about 20,000 Daltons and about 70,000 Daltons. The intermediate molecular weight polyester is heated and a solvent is added prior to or during the heating process to produce a composition comprising a macrocyclic oligoester.

The composition comprising macrocyclic oligoester includes, for example, a mixture of macrocyclic oligoesters and linear oligoesters. An optional step is to separate a macrocyclic oligoester from the composition comprising the macrocyclic oligoester.

[0009] Methods of the invention minimize operations and eliminate the need for costly equipment. Of the steps used to manufacture linear polyesters, only those steps necessary for ultimate recovery of macrocyclic oligomers are employed and integrated with the operations necessary to recover a macrocyclic oligomer composition. For example, the use of costly melt reactors is unnecessary. Later steps in prior art polyester preparation, in particular steps necessary to produce a high molecular weight product, are eliminated thereby providing a product adequate for conversion to macrocyclic oligomers without significant loss in yield.

[0010] Methods of the invention also permit the use of equipment that transports low viscosity materials, whereby these methods are less expensive than prior art alternatives. According to the invention, low viscosity intermediate molecular weight polyesters are employed to make macrocyclic oligoesters. However, compared to the above-described methods employing high molecular weight polymers, methods of the present invention employing intermediate molecular weight polyesters have an increased number of linear polyesters with uncyclizable end groups remaining after cyclization. To promote further reaction to form macrocyclic oligoesters from intermediate molecular weight polyesters, it may be desirable to remove an uncyclizable end group, e.g., a hydroxyalkoxy group, from the linear polyester to create an intermediate molecular weight polyester capable of forming a macrocyclic oligoester. Removal of an end group results in by-product diol, which may be the starting material diol, i.e., the first compound.

[0011] In one embodiment, one or more solvents are employed for removal of by-product diol(s) by distillation, as the by-product diol(s) should be removed before cyclization takes place. The distillation may be, for example, azeotropic distillation, or distills or co-distills of the by-product diols may distill off at a temperature below the boiling point of the solvent. Thus, energy- and equipment-intensive methods, for example, melt reaction, necessitated by the high melt viscosity of the product are replaced by a simple distillation. In addition, the use of solvent reduces the viscosity of the macrocyclic polyester product, which enables the

process to employ less costly equipment that is capable of transporting a low viscosity material.

[0012] Thereafter, the removed end groups, which typically result in by-product diols, may be transported and purged as waste from the process. Alternatively, a recycling step may be employed to reuse the by-product diol as a reactant in the process. Likewise, the volume demand on an existing recycling step may increase in order to transport the by-product diol created during the process. Despite the addition of such a recycling step or the additional volume demand on an existing recycling step, methods of making macrocyclic oligoesters from low viscosity intermediate molecular weight polyesters can be more cost-effective than prior methods. The cost benefit is due in part to the ability to employ simple distillation in place of expensive finishing steps. Also, transporting low viscosity polyesters is less costly than transporting high viscosity material. Macrocyclic oligoester production methods according to the invention can be conducted continuously, semi-continuously, according to a batch methodology, or a combination thereof.

[0013] In another aspect, an embodiment of a method for preparing a macrocyclic oligoester composition includes providing an intermediate molecular weight polyester, a solvent, and a catalyst. The catalyst may comprise, for example, a tin compound or a titanate compound. The intermediate molecular weight polyester, solvent, and a catalyst are heated to produce a composition comprising a macrocyclic oligoester. The method may further include separating the macrocyclic oligoester from the composition comprising the macrocyclic oligoester.

[0014] The foregoing, and other features and advantages of the invention, as well as the invention itself, will be more fully understood from the description, drawings, and claims which follow.

#### Brief Description of Figures

[0015] FIG. 1 is a schematic flow diagram of an embodiment of a method of the invention for making a macrocyclic oligoester.

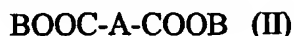
[0016] FIG. 2 is a schematic flow diagram of another embodiment of a method of the invention for making a macrocyclic oligoester.

### Description

[0017] In one aspect, a method of the invention for preparing macrocyclic oligoesters generally includes contacting a first compound having a structural formula:



where R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group, with a second compound having a structural formula:



where A is a divalent aromatic group or an alicyclic group, and B is hydrogen or an alkyl group. The compounds of formulas (I) and (II) are contacted in the presence of a first catalyst to produce a composition comprising a hydroxyalkyl-terminated polyester oligomer. Heating the composition comprising the hydroxyalkyl-terminated polyester oligomer at a reduced pressure produces a composition comprising an intermediate molecular weight polyester. Heating the composition comprising the intermediate molecular weight polyester in the presence of a solvent produces a composition comprising a macrocyclic oligoester. Optionally, the macrocyclic oligoester is separated from the composition comprising the macrocyclic oligoester.

[0018] Referring to FIG. 1, in which a flow diagram depicts an embodiment of a method of the invention, an intermediate molecular weight polyester is employed to prepare a composition comprising a macrocyclic oligoester. A first compound 10 is contacted with a second compound 14 in the presence of a first catalyst 18 (STEP 80) to produce a composition comprising a hydroxyalkyl-terminated polyester oligomer 90.

[0019] The first compound 10 has the structural formula HO-R-OH. The substituent "R" may be, for example, an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group. The mono- or polyoxyalkylene group may include between about 2 and about 8 carbon atoms. In one embodiment, the polyoxyalkylene group includes a polyoxyalkylene radical. In some embodiments, the alkylene is ethylene  $-(\text{CH}_2\text{CH}_2)-$ , tetramethylene  $-((\text{CH}_2)_4)-$ , or a mixture thereof. 1,2-Ethanediol (R= ethylene) may be employed when producing the homopolymer, poly(ethylene terephthalate) ("PET"). Alternatively, to produce poly(butylene terephthalate) ("PBT"), 1,4 butanediol (R= tetramethylene) may be employed. A mixture of these

compounds may be used to produce a copolymer, for example, the copolymer poly(butylene terephthalate)/poly(ethylene terephthalate) ("PBT/PET").

[0020] The first compound 10 may be an aliphatic diol. In another embodiment, a mixture of diols may include only alkylene glycols such as, for example, ethylene glycol and 1,4-butanediol, or may additionally include ether diols such as diethylene glycol, the product of which is employed to produce a macrocyclic copolyester oligomer.

[0021] In one embodiment, the second compound 14 has the structural formula  $\text{BOOC-A-COOB}$ . The substituent "A" may be, for example, a divalent aromatic group or an alicyclic group. The alicyclic group may be an alicyclic radical, for example, a meta-linked or a para-linked monocyclic radical. In one embodiment, the para-linked aromatic group is a para-linked benzene group. In another embodiment, the substituent "A" is a meta- or para-phenylene or a mixture thereof. The substituent "B" may be, for example, hydrogen or an alkyl group. The alkyl group preferably has from 1 to 6 carbon atoms. Commonly used alkyl groups include methyl and ethyl.

[0022] In an exemplary embodiment, the second compound 14 includes one or more aromatic dicarboxylic acids or alkyl esters thereof. The dicarboxylic acid or acids may be employed in their free acid form or, preferably, in the form of an alkyl ester, most often in the form of a diester, for example, a di-( $\text{C}_{1-4}$  alkyl) ester such as dimethyl terephthalate. Thus, the preferred polyesters are poly(butylene terephthalate) ("PBT"), poly(ethylene terephthalate) ("PET"), the corresponding isophthalates, and copolyesters thereof, i.e., PBT/PET.

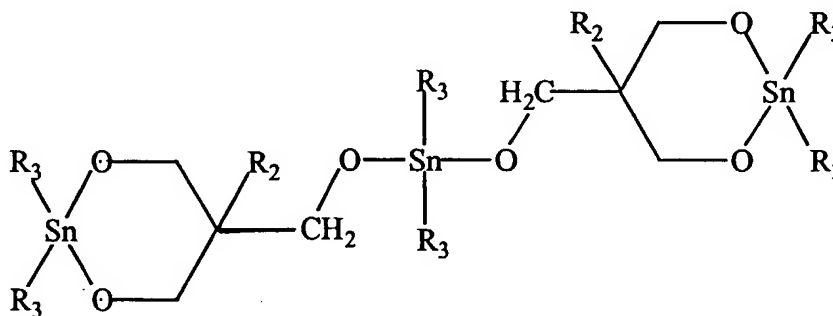
[0023] When contacting the first compound 10 and the second compound 14 (STEP 80), any conditions may be employed so long as they promote the reaction. Such conditions may include, for example, providing the first compound 10 and the second compound 14 in a molar ratio between about 1.05:1 and about 1.5:1. An amount of catalyst 18 in the range of from about 0.1 mole percent to about 5 mole percent based on the first compound may be provided to promote the reaction conducted in STEP 80. In some embodiments, the amount of catalyst ranges between about 1 mole percent to about 5 mole percent based on the first compound.

[0024] When an ester such as dimethyl terephthalate is employed, it is preferred to employ a temperature at which the displaced alkanol will be removed by distillation, thus driving the reaction toward formation of the desired hydroxyalkyl-terminated polyester oligomer composition 90. In one embodiment, the first compound 10 contacts the second compound 14 and the temperature is held between about 140°C and about 200°C. In another embodiment, the first compound 10 contacts the second compound 14 and the temperature is held between about 160°C and about 180°C. In yet another embodiment, the first compound 10 contacts the second compound 14 and the temperature is held between about 180°C and about 200°C.

[0025] The catalyst(s) employed in the practice of the invention are adapted to polyester preparation. More specifically, catalysts employed in the invention are those that are capable of catalyzing a transesterification polymerization of a macrocyclic oligoester with a dihydroxyl-functionalized polymer. Numerous such catalysts are known in the art. The catalysts may comprise a tin compound or a titanate compound. As with state-of-the-art processes for polymerizing macrocyclic oligoesters, organotin and organotitanate compounds are the preferred catalysts, although other catalysts may be used. One or more catalysts may be used together or sequentially.

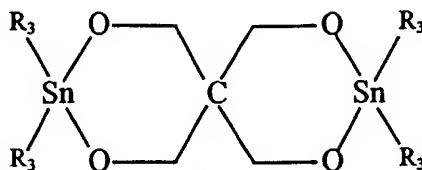
[0026] Illustrative examples of classes of tin compounds that may be used in the invention include monoalkyltin(IV) hydroxide oxides, monoalkyltin(IV) chloride dihydroxides, dialkyltin(IV) oxides, bistralkyltin(IV) oxides, monoalkyltin(IV) trisalkoxides, dialkyltin(IV) dialkoxides, trialkyltin(IV) alkoxides, tin compounds having the formula (III):

(III)



and tin compounds having the formula (IV):

(IV)

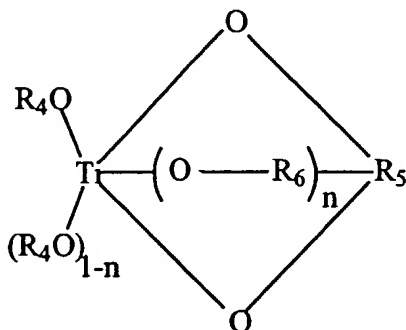


wherein  $\text{R}_2$  is a  $\text{C}_{1-4}$  primary alkyl group, and  $\text{R}_3$  is  $\text{C}_{1-10}$  alkyl group.

[0027] Specific examples of organotin compounds that may be used in this invention include dibutyltin dioxide, 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclododecane, *n*-butyltin(IV) chloride dihydroxide, di-*n*-butyltin(IV) oxide, dibutyltin dioxide, di-*n*-octyltin oxide, *n*-butyltin tri-*n*-butoxide, di-*n*-butyltin(IV) di-*n*-butoxide, 2,2-di-*n*-butyl-2-stanna-1,3-dioxacycloheptane, and tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.* In addition, tin catalysts, and other catalysts including titanate compounds described in commonly owned U.S.S.N. 09/754,943, may be used in the polymerization reaction.

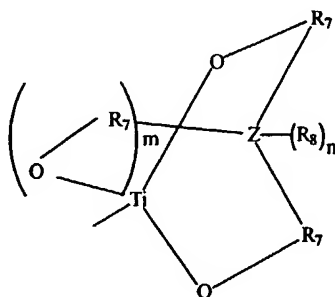
[0028] Titanate compounds may be used in the invention and illustrative examples of titanate compounds include tetraalkyl titanates (e.g., tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, and tetrabutyl titanate), isopropyl titanate, titanate ester, titanate tetraalkoxide. Other illustrative examples include (a) titanate compounds having the formula (V):

(V)



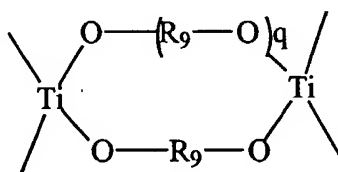
wherein each  $R_4$  is independently an alkyl group, or the two  $R_4$  groups taken together form a divalent aliphatic hydrocarbon group;  $R_5$  is a  $C_{2-10}$  divalent or trivalent aliphatic hydrocarbon group;  $R_6$  is a methylene or ethylene group; and  $n$  is 0 or 1, (b) titanate ester compounds having at least one moiety of the formula (VI):

(VI)



wherein each  $R_7$  is independently a  $C_{2-3}$  alkylene group;  $Z$  is O or N;  $R_8$  is a  $C_{1-6}$  alkyl group or unsubstituted or substituted phenyl group; provided when  $Z$  is O,  $m=n=0$ , and when  $Z$  is N,  $m=0$  or 1 and  $m+n=1$ , and (c) titanate ester compounds having at least one moiety of the formula (VII):

(VII)



wherein each  $R_9$  is independently a  $C_{2-6}$  alkylene group; and  $q$  is 0 or 1.

[0029] Referring again to FIG. 1, as described previously, the first compound 10 and the second compound 14 are contacted (STEP 80) in the presence of an above-described catalyst 18 to produce a compound comprising a hydroxyalkyl-terminated polyester oligomer 90. The condensation reaction which takes place in STEP 80 can be considered complete when no remaining alkanol, usually methanol, is found in the distillate. It is usually found that some diol is removed with the alkanol, but diol removal is primarily the function of the later heating steps, (e.g., STEP 100 and STEP 120) described below.



[0030] The hydroxyalkyl-terminated polyester oligomer 90 is heated in a first heating step (STEP 100) to produce a composition comprising an intermediate molecular weight polyester 110. In one embodiment, the hydroxyalkyl-terminated polyester oligomer 90 composition is heated under reduced pressure (i.e., pressure less than atmospheric pressure) whereupon further condensation takes place with removal of diol by distillation, producing a composition comprising an intermediate molecular weight polyester 110. Temperatures in the range of about 180-275°C and pressures in the range of about 5-625 torr are typically employed in this heating step (STEP 100).

[0031] In one embodiment, the one or more solvents are employed for removal of by-product diol by distillation, where the by-product diol should be removed before cyclization takes place. The distillation may be, for example, azeotropic distillation. Alternatively, distills or co-distills of the by-product diol may distill off at a temperature below the boiling point of the solvent. Preferably, the boiling point of the selected solvent is higher than the boiling point of the diol that is being removed. Thus, energy- and equipment-intensive methods such as, for example, melt reaction, necessitated by the high melt viscosity of the product are replaced by a simple distillation. The added solvent reduces the viscosity of the macrocyclic polyester product, which enables less costly equipment, which is capable of transporting low viscosity product to be employed in this process.

[0032] In some embodiments, during the first heating step (STEP 100) a second catalyst is added to the composition comprising hydroxyalkyl-terminated polyester oligomer 90. One or more of the above-described catalysts may be employed. In one embodiment, the second catalyst that is added in the heating step (STEP 100) is identical to the first catalyst 18 that was introduced in the prior step (STEP 80). The second catalyst may be added, for example, to speed the rate of reaction or to replenish inactivated catalyst.

[0033] In another embodiment, the first heating step (STEP 100) is accomplished in multiple stages. For example, first and second stages may be employed. In an exemplary embodiment, the first stage includes heating at a temperature between about 175°C and about 200°C and a reduced pressure of between about 550 torr and about 625 torr. Thereafter, the second stage includes heating at an increased temperature between about 225°C and about 275°C and a decreased reduced pressure of between about 5 torr and about 15 torr.

**[0034]** In yet another embodiment, the heating step (STEP 100) is conducted until polymerization is about 95-98% complete, e.g., as estimated by the proportion of diol (i.e., the first compound 10) removed by distillation. In one embodiment, aliphatic diol is removed via distillation. In the first heating step (STEP 100), it is not necessary to remove all traces of diol, as any remaining diol is efficiently removed in the second heating step (STEP 120) as described hereinafter. The product of the first heating step (STEP 100) is a composition comprising intermediate molecular weight polyester 110. The intermediate molecular weight polyester 110 may be predominantly linear and in some embodiments it may contain hydroxyalkyl end groups in minor proportion.

**[0035]** In one embodiment, the molecular weight of the intermediate molecular weight polyester is between about 20,000 Daltons and about 70,000 Daltons. In another embodiment, the molecular weight of the intermediate molecular weight polyester is between about 30,000 Daltons and about 60,000 Daltons. In yet another embodiment, the molecular weight of the intermediate molecular weight polyester is between about 40,000 Daltons and about 50,000 Daltons.

**[0036]** The intermediate molecular weight polyester 110 is heated and a solvent 114 is added (STEP 120) to form a composition comprising a macrocyclic oligoester 130. In one embodiment, the second heating step (STEP 120) is employed to remove remaining hydroxyalkyl end groups creating one or more appropriate reactive sites to cause cyclization to form macrocyclic oligomers. The method employs a solvent 114 for three purposes: to lower the viscosity of the mixture, to aid in the removal of by-product diol by distillation, and to provide high dilution conditions which promote cyclization. The hydroxyalkyl end groups that were converted to by-product diol may be recycled within the process by adding the by-product diol to the first compound 10 in STEP 80. Alternatively, the by-product diol may be removed as waste. The intermediate molecular weight polyester 110 may be heated to the reflux temperature of the added solvent 114, for example, a temperature between about 150°C and about 200°C.

**[0037]** In some embodiments, a diol, i.e., a by-product diol, is produced in the second heating step (STEP 120). The solvent 114 that is employed is capable of forming a mixture

with the by-product diol, and removes the last traces of the by-product diol by distillation to afford a macrocyclic oligoester composition 130.

[0038] In certain embodiments, it may be desirable to add the solvent in two stages. In a first stage, the solvent is added to assist in the removal of by-product diol that results from the removal of uncyclized end groups from linear polyesters. In the first stage, the amount of intermediate molecular weight polyester in the mixture may increase. Also, the molecular weight of the intermediate molecular weight polyester may increase. In a second stage more solvent is added to provide dilute conditions that promote cyclization and may increase the yield of macrocyclic oligoesters.

[0039] Solvents that may be used may be capable of forming an azeotropic mixture with the by-product diol to be removed, for example, with 1,4-butanediol in the case of PBT processing. Alternative solvents may be employed so that the distills or co-distills may distill off at a temperature below the temperature of the solvent.

[0040] In one embodiment, the solvent 114 comprises a halogenated aromatic hydrocarbon, for example, ortho-dichlorobenzene. Ortho-dichlorobenzene is particularly useful for treatment of PBT. In another embodiment, the solvent 114 is added in an amount to produce a mixture containing from about 5% to about 25% solids by weight, that is, about 5-25% of linear and cyclic polyesters. The mixture may be a solution. In yet another embodiment, the solvent 114 is added to dilute the composition comprising intermediate molecular weight polyester 110 to about one tenth normal (0.1 N) concentration. The added solvent 114 provides dilute conditions that promote cyclization. By cyclizing intermediate molecular weight oligomers rather than high molecular weight oligomers, the method avoids reaction kinetics that require large sized reactors (i.e., second order kinetics or higher).

[0041] In some embodiments, the cyclization yield is generally dependent upon the dilution of macrocyclic oligoester. More dilute conditions typically provide a higher yield of cyclics in the composition comprising macrocyclic oligoesters 130. Table 1 illustrates the relationship between dilution conditions, i.e., the molar concentration of macrocyclic oligoesters based on a monomer molecular weight of 220 Daltons PBT where a terephthalic acid derivative solvent is employed, and yield (see *e.g.* Table 1). In Table 1, the percentage

yield of macrocyclic oligoester was analytically determined using HPLC analysis, assuming a molecular weight of 220 Daltons. Suitable HPLC equipment is available from Hewlett Packard (Palo Alto, CA).

(TABLE 1)

Experiment Number	Molar Concentration (M)	Percentage Yield (%)
1	0.049	72
2	0.06	65.6
3	0.076	66.6
4	0.091	54.1
5	0.125	42.7
6	0.195	27.9

[0042] In some embodiments, a third catalyst is added in the second heating step (STEP 120) to the composition comprising intermediate molecular weight polyester. The catalyst may be any compound catalytically effective for depolymerization of a linear polyester to macrocyclic oligomer species. Also useful are catalysts effective for polymerization of macrocyclic oligomers to linear polyesters, since this reaction is the reverse of the depolymerization reaction and employs the same catalysts with changes in other conditions such as dilution. Numerous compounds with such activity are known in the art, for example, the titanium and tin compounds described in U.S. Patent Nos. 5,407,984; 5,668,186; 5,389,719; 5,466,744; 5,527,976; 5,648,454; 5,661,214; and 5,710,086.

[0043] Among the compounds active as depolymerization catalysts, as noted in the aforementioned U.S. Patent No. 5,466,744, are the tetraalkyl titanates employed in contacting step (STEP 80) and the first heating step (STEP 100) of the present invention. Thus, it may

be possible to conduct the second heating step (STEP 120) without addition of further catalyst. It is sometimes advisable to replenish the catalyst, however, since some loss of activity may occur in the prior steps (STEP 80 and STEP 100). Whether or not catalyst replenishment is necessary can be determined by monitoring the rate of the reaction. For example, in some embodiments, catalyst is added in the first step (STEP 80) and additional catalyst is added in the second heating step (STEP 120), upon reduction of the reaction rate.

[0044] The amount of catalyst, if any, added in the second heating step (STEP 120) may be identical or similar to the quantity of catalyst introduced in the first step (STEP 80). In an exemplary embodiment, the type of catalyst that is added in the second heating step (STEP 120) is the same as the type of catalyst that is added in the first step (STEP 80). In another embodiment, the type of catalyst added in the second heating step (STEP 120) is different than the type of catalyst that was added in the first step (STEP 80).

[0045] Upon completion of the second heating step (STEP 120), the composition comprising a macrocyclic oligoester is formed. In one embodiment, water is added during the second solvent removal. In another embodiment, water is added after the second heating step. The quantity of water that may be added may be the molar equivalent of the total catalyst used. For example, where a total of 10 mmol of catalyst have been used in the process (STEP 80, STEP 100, and STEP 120) then 10 mmol of water may be added upon completion of STEP 120 to quench the reaction mixture and terminate the reaction.

[0046] In yet another embodiment, an additional step (STEP 140) is conducted to separate macrocyclic oligoesters from the composition comprising macrocyclic oligoesters. In some embodiments, the composition comprising macrocyclic oligoesters includes macrocyclic oligomers and linear oligomers. In some embodiments, linear polyester is separated from the composition comprising macrocyclic oligoester resulting in a material in which the principal constituents are macrocyclic oligoester, normally a mixture of oligoesters of varying degrees of polymerization where those between about 2 and about 7 are present in greatest proportion.

[0047] Separation methods employed in the separating step (STEP 140) to remove the linear polyester may be selected from such operations known in the art as filtration, filtration

at a reduced temperature, and adsorption. For example, the mixture may be cooled and filtered to remove linears. The filtrate may then be subjected to adsorption using alumina to remove final traces of linears, alternatively, adsorption may be accomplished using column chromatography with silica to remove final traces of linears. After the final traces of linears are removed, the macrocyclic oligoesters may be isolated by precipitation with a non-solvent, typically an aliphatic hydrocarbon, and preferably a C<sub>6-10</sub> hydrocarbon such as heptane.

[0048] In one exemplary embodiment, a method for preparing a macrocyclic oligoester composition includes conducting a reaction between at least one aliphatic diol and at least one aromatic dicarboxylic acid or alkyl ester thereof as reactants in the presence of a catalyst, to produce a hydroxyalkyl-terminated polyester oligomer composition (STEP 80). The method includes heating the hydroxyalkyl-terminated polyester oligomer under reduced pressure to distill off aliphatic diol, thereby producing an intermediate molecular weight polyester (STEP 100). The method includes heating the intermediate molecular weight polyester in the presence of a catalyst and a solvent that is capable of forming a mixture with the aliphatic diol. The last traces of the aliphatic diol are removed by distillation to afford a composition comprising a macrocyclic oligoester (STEP 120). The method includes removing linear polyester from the macrocyclic oligomer-enriched polyester composition (STEP 140).

[0049] In one embodiment, the reactants in the reaction (STEP 80) are ethylene glycol and/or 1,4-butanediol and dimethyl terephthalate, where these reactants yield a PBT/PET copolymer. In another embodiment, 1,4-butanediol is reacted with dimethyl terephthalate to yield a PBT homopolymer. In another embodiment, the catalyst 18 is a titanate ester. In another embodiment, the titanate ester is tetraisopropyl titanate. In another embodiment, the temperature of the reaction (STEP 80) is one at which displaced methanol is removed by distillation. In another embodiment, the temperature of the reaction step (STEP 80) is in the range of about 140-200°C.

[0050] In one embodiment, the solvent employed in the second heating step (STEP 120) is a halogenated aromatic hydrocarbon. In another embodiment, the solvent is *ortho*-dichlorobenzene. In one embodiment, the catalyst employed in the reaction (STEP 80) is also active in the second heating step (STEP 120). In another embodiment, additional catalyst is added in the second heating step (STEP 120). In another embodiment, the amount

of solvent employed is an amount to produce a solution containing about 5-25% solids by weight. In another embodiment, the method includes a quenching operation following the second heating step (STEP 120). In one embodiment, the separation step (STEP 140) includes filtration or adsorption.

[0051] Referring to FIG. 2, in another aspect of the invention, a method for preparing a macrocyclic oligoester composition includes providing an intermediate molecular weight polyester, providing a solvent and a catalyst (STEP 210). In some embodiments, a composition comprising intermediate molecular weight polyester is provided. As described above, in one embodiment, the intermediate molecular weight polyester has a molecular weight between about 20,000 Daltons and about 70,000 Daltons. A solvent 214 and a catalyst 218 are added.

[0052] The intermediate molecular weight polyester, solvent 214, and catalyst 218 are heated (STEP 220) to produce a composition comprising a macrocyclic oligoester 230. In this step (STEP 220), as described above in relation to the second heating step of FIG. 1 (STEP 120), the added solvent 214 aids in the removal of by-product diol by distillation, provides high dilution conditions which promote cyclization, and lower the viscosity of the mixture.

[0053] In certain embodiments, it may be desirable to add the solvent in two stages. In a first stage, solvent is added to assist in the removal of by-product diol that results from the removal of uncyclized end groups from linear polyesters. In the first stage, the amount of intermediate molecular weight polyester in the mixture may increase. Also, the molecular weight of the intermediate molecular weight polyester may increase. In a second stage more solvent is added to provide dilute conditions that promote cyclization and may increase the yield of macrocyclic oligoesters.

[0054] The by-product diol may be recycled within the process by contacting the by-product diol to the second compound 14 in (STEP 80). Alternatively the by-product diol may be removed as waste. The by-product diol may be, for example, 1,4-butane diol. The catalyst 218 that is employed affects the rate of reaction. The type and quantity of catalyst 218 that

may be employed may be the type and quantity of catalyst 18 that is described above with regard to FIG. 1.

[0055] Similarly, the type and quantity of solvent 214 that may be employed in this embodiment (STEP 220) is the same as the type and quantity of solvent 114 that is described above in the second heating step of FIG. 1 (STEP 120). For example, the solvent 214 may be added in an amount to produce a solution containing from about 5% to about 25% solids by weight. The solvent 214 that may be added may include, for example, 1,4-butanediol, a halogenated aromatic hydrocarbon, or a halogenated aromatic hydrocarbon comprising ortho-dichlorobenzene. The intermediate molecular weight polyester may be heated to a temperature between about 150°C and about 200°C.

[0056] In one embodiment, the method is complete when the composition comprising macrocyclic oligoester 230 is formed, which is upon completion of the heating step (STEP 220). In another embodiment, water is added after the heating step to quench the reaction mixture and terminate the reaction prior to solvent removal. The quantity of water that may be added may be the molar equivalent of the total catalyst used. For example, where a total of 10 mmol of catalyst have been used in the process (STEP 210 and STEP 220) then 10 mmol of water may be added upon completion of (STEP 220) to quench the reaction mixture and terminate the reaction.

[0057] In yet another embodiment, a separation step (STEP 240) may be employed to separate macrocyclic oligoesters from the composition comprising macrocyclic oligoesters 230. In some embodiments, linear polyester is separated from the composition comprising macrocyclic oligoester 230 to leave a material in which the principal constituents are macrocyclic oligoester, normally a mixture of oligoesters of varying degrees of polymerization where those between about 2 and about 7 are present in greatest proportion. Separation methods employed in the separation step to remove the linear polyester may be selected from such operations known in the art as filtration, filtration at a reduced temperature, and adsorption.

[0058] The invention is illustrated further by the following non-limiting examples. In the examples, each of the steps of FIG. 1 (STEPS 80, 100, 120, and 140) is described in a



separate example. Frequently, however, these steps can and will be performed as a single sequence.

#### EXAMPLE 1

[0059] As an example of STEP 80, a 3-necked flask fitted with a stirrer, thermometer and vacuum-jacketed Vigreux distillation column, charged with 100 g (515 mmol) of dimethyl terephthalate, 72.21 g (802 mmol) of 1,4-butanediol and 7.1 g (25 mmol) of isopropyl titanate. Vigreux distillation column obtained from Ace Glass, Incorporated (Vineland, NJ). The resulting mixture was heated over 90 minutes to 175°C, with stirring, as methanol was removed by distillation. At the end of this period, some 1,4-butanediol was also removed. The product was the desired 4-hydroxybutyl-terminated PBT oligomer composition as analytically determined by HPLC. The analysis employed a Hewlett Packard HPLC, Model 1110 (Palo Alto, CA) equipped with a diode array detector set at 254 nM, a Zorbax C-8 reverse phase column maintained at 40°C with a solvent gradient of acetonitrile and water.

#### EXAMPLE 2

[0060] As an example of STEP 100, the pressure in the flask of Example 1 was reduced to 600 torr and distillation was continued at 195°C for 60 minutes. The pressure was reduced further as distillation of 1,4-butanediol was continued at 215°C/150 torr for 45 min, 230°C/40 torr for 40 min and 240°C/10 torr for 40 min. The flask was cooled to 180°C and returned to atmospheric pressure, yielding a PBT of intermediate molecular weight of about 20,000 Daltons weighing 113 grams. The molecular weight of the intermediate molecular weight PBT is determined by gel permeation chromatography (GPC) relative to polystyrene standards using an Hewlett Packard HPLC, Model 1050 (Palo Alto, CA). The HPLC is equipped with a fixed wavelength detector set at 254 nM, two linear Phenogel GPC columns where each column measures 300 mm x 7.8 mm and the Phenogel has a 5 micron particle size and maintained at a temperature of 40°C. The solvent, chloroform (CHCl<sub>3</sub>) is passed through the GPC columns at a rate of 1.0mL/min.

### EXAMPLE 3

**[0061]** As an example of STEP 120 or STEP 220, ortho-dichlorobenzene (o-DCB), 1,300 ml, was added to the flask of Example 3 to produce a solution with 10% solids concentration. Heating under reflux was begun and o-DCB was removed by distillation. Samples of the product were periodically removed and their average molecular weight were determined as described above, by GPC relative to polystyrene standards using an Hewlett Packard HPLC, Model 1050 (Palo Alto, CA), and when the molecular weight value reached 100,000 Daltons, an additional 6.84 liters of o-DCB was added and heating under reflux was resumed for 1.5 hrs. The reaction was then quenched by the addition of 2 ml of water and 70% of the o-DCB was removed with 1,4-butanediol by azeotropic distillation, yielding a PBT composition enriched in macrocyclic oligomer content as analytically determined according to the above described methods by HPLC employing a Hewlett Packard HPLC, Model 1110 (Palo Alto, CA).

### EXAMPLE 4

**[0062]** As an example of STEP 140 or STEP 240, the composition of Example 3 was cooled to 70°C and insoluble linear polyester was removed by filtration using a Buchner funnel under vacuum conditions. The filtrate was passed through an alumina column to remove additional linears including residual end groups; combined linears could be recycled for conversion to cyclics or conversion by depolymerization to dimethyl terephthalate. Suitable alumina is alumina with Brockman Activity Grade I available from Whatman (Clifton, NJ) that is packed into a standard laboratory column.

**[0063]** Further concentration to 50% solids was effected by o-DCB stripping which was determined effected when a quantity of o-DCB was condensed off of the process. Heptane was introduced in a threefold volume amount, resulting in the precipitation of the desired macrocyclic PBT oligomer mixture, which was removed by filtration and dried in vacuum. The macrocyclic PBT could be polymerized by contact with a stannoxane catalyst at 190°C.

**[0064]** In the following example, the steps (STEPS 210 and 220) of FIG. 2 are described.

## EXAMPLE 5

[0065] As an example of STEP 210, 2.15 grams of PBT of intermediate molecular weight, 42,000 Daltons, is provided. The molecular weight of the intermediate molecular weight PBT was determined by gel permeation chromatography (GPC) relative to polystyrene standards according to the above described methods employing a Hewlett Packard HPLC, Model 1050. 143 grams of the solvent o-DCB was added to the 2.15 grams of intermediate molecular weight PBT. This stirred reaction mixture was heated to reflux, where 15 grams of o-DCB was removed by azeotropic distillation to complete the drying of the 0.1 Molar mixture of PBT and o-DCB and to form a dry solution. Then 0.49 mmole of organo titanate catalyst was added to the dry solution.

[0066] In STEP 220, the PBT catalyst and dry solution was heated at reflux for a period of 30 min. to produce a macrocyclic oligoester. The production of macrocyclic oligoester was confirmed when HPLC analysis assuming a molecular weight of 220 Daltons demonstrated that macrocyclic oligoester in the form of an oligomeric cyclic array was present at a concentration of 9.3 g/L, which is a 48% yield. The analysis employed the above-described Hewlett Packard HPLC, Model 1110.

[0067] The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The foregoing embodiments are therefore to be considered in all respects illustrative rather than limiting on the invention described herein. Scope of the invention is thus indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

[0068] Each of the patent documents and scientific publications disclosed hereinabove is incorporated by reference herein.

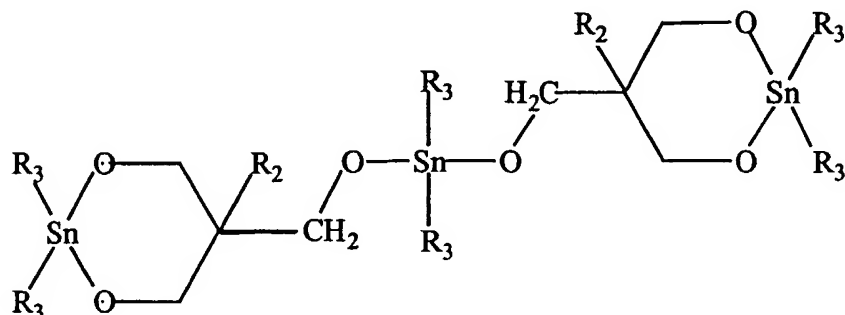
## CLAIMS

What is claimed is:

- 1 1. A method for preparing a macrocyclic oligoester comprising the steps of:
  - 2 (a) contacting a first compound having a structural formula:  
3 
$$\text{HO-R-OH (I)}$$
  
4 wherein  
5 R is an alkylene, a cycloalkylene, or a mono- or a  
6 polyoxyalkylene group;  
7 with a second compound having a structural formula:  
8 
$$\text{BOOC-A-COOB (II)}$$
  
9 wherein  
10 A is a divalent aromatic group or an alicyclic group, and  
11 B is hydrogen or an alkyl group;  
12 in the presence of a first catalyst to produce a composition comprising a  
13 hydroxyalkyl-terminated polyester oligomer;  
14 (b) heating the composition comprising the hydroxyalkyl-terminated polyester  
15 oligomer at a reduced pressure to produce a composition comprising an intermediate  
16 molecular weight polyester; and  
17 (c) heating the composition comprising the intermediate molecular weight polyester in  
18 the presence of a solvent to produce a composition comprising a macrocyclic oligoester.
  - 1 2. The method of claim 1 wherein R is ethylene, tetramethylene, or a mixture thereof.
  - 1 3. The method of claim 1 wherein the mono- or polyoxyalkylene group comprises  
2 between 2 and 8 carbon atoms.
  - 1 4. The method of claim 1 wherein the alicyclic group is a para-linked aromatic group.
  - 1 5. The method of claim 4 wherein the para-linked aromatic group is a para-linked  
2 benzene group.
  - 1 6. The method of claim 1 wherein the first catalyst comprises a tin compound or a  
2 titanate compound.
  - 1 7. The method of claim 6 wherein the tin compound comprises a compound selected  
2 from the group consisting of: (a) monoalkyltin(IV) hydroxide oxide, (b) monoalkyltin(IV)  
3 chloride dihydroxide, (c) dialkyltin(IV) oxide, (d) bistralkyltin(IV) oxide, (e)

4 monoalkyltin(IV) trisalkoxide, (f) dialkyltin(IV) dialkoxide, (g) trialkyltin(IV) alkoxide, (h) a  
5 tin compound having the formula:

6 (III)



7

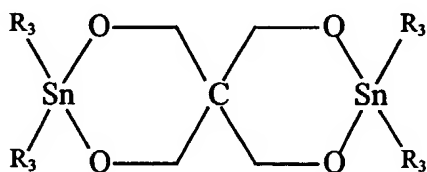
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9 and

10 (i) a tin compound having the formula:

11 (IV)

12



13

14

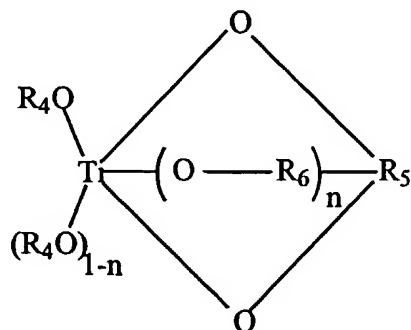
15 wherein:

16 R<sub>2</sub> is a C<sub>1-4</sub> primary alkyl group, and

17 R<sub>3</sub> is C<sub>1-10</sub> alkyl group.

1 8. The method of claim 6 wherein the titanate compound comprises a compound selected  
2 from the group consisting of: (a) tetraisopropyl titanate, (b) isopropyl titanate, (c) tetraalkyl  
3 titanate, (d) titanate tetraalkoxide, (e) a titanate compound having the formula:

4 (V)



5

6 wherein:

each  $R_4$  is independently an alkyl group, or the two  $R_4$  groups taken together form a divalent aliphatic hydrocarbon group;

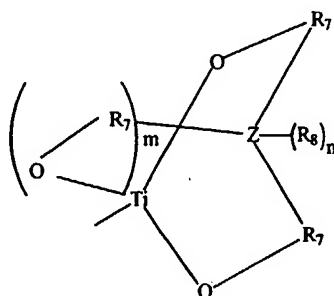
$R_5$  is a  $C_{2-10}$  divalent or trivalent aliphatic hydrocarbon group;

$R_6$  is a methylene or ethylene group; and

$n$  is 0 or 1,

(f) a titanate ester compound having at least one moiety of the formula:

(VI)



wherein:

each  $R_7$  is independently a  $C_{2-3}$  alkylene group;

$Z$  is O or N;

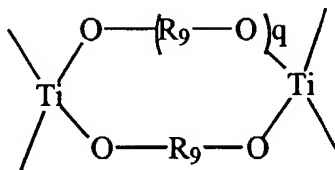
$R_8$  is a  $C_{1-6}$  alkyl group or unsubstituted or substituted phenyl group;

provided when  $Z$  is O,  $m=n=0$ , and when  $Z$  is N,  $m=0$  or 1 and  $m+n=1$ ,

and

(g) a titanate ester compound having at least one moiety of the formula:

(VII)



wherein:

each  $R_9$  is independently a  $C_{2-6}$  alkylene group;

and  $q$  is 0 or 1.

9. The method of claim 1 wherein the molar ratio of the first compound to the second compound is between about 1.05:1 and about 1.5:1.

10. The method of claim 1 wherein the first catalyst is present in an amount from about 1 mole percent to about 5 mole percent of the first compound.

11. The method of claim 1 wherein step (a) further comprises contacting the first compound and the second compound at a temperature between about 140°C and about 200°C.

- 1 12. The method of claim 1 wherein step (b) further comprises adding a second catalyst to  
2 the composition comprising the hydroxyalkyl-terminated polyester oligomer.
- 1 13. The method of claim 12 wherein the first catalyst and the second catalyst are identical.
- 1 14. The method of claim 1 wherein step (b) comprises heating at reduced temperature  
2 between about 180°C and about 275°C.
- 1 15. The method of claim 1 wherein step (b) comprises heating at a reduced pressure  
2 between about 5 torr and about 625 torr.
- 1 16. The method of claim 1 wherein the step (b) comprises a first stage and a second stage.
- 1 17. The method of claim 16 wherein the first stage comprises heating at a temperature  
2 between about 175°C and about 200°C and a reduced pressure of between about 550 torr and  
3 about 625 torr, and the second stage comprises heating at a temperature between about 225°C  
4 and about 275°C and a reduced pressure of between about 5 torr and about 15 torr.
- 1 18. The method of claim 1 wherein the product of step (b) has a percentage yield between  
2 about 95% and about 98%.
- 1 19. The method of claim 1 wherein the molecular weight of the intermediate molecular  
2 weight polyester is between about 20,000 Daltons and about 70,000 Daltons.
- 1 20. The method of claim 1 wherein the molecular weight of the intermediate molecular  
2 weight polyester is between about 30,000 Daltons and about 60,000 Daltons.
- 1 21. The method of claim 1 wherein the molecular weight of the intermediate molecular  
2 weight polyester is between about 40,000 Daltons and about 50,000 Daltons.
- 1 22. The method of claim 1 wherein step (c) comprises heating at a temperature between  
2 about 150°C and about 200°C.
- 1 23. The method of claim 1 wherein step (c) comprises adding a third catalyst to the  
2 composition comprising the intermediate molecular weight polyester.
- 1 24. The method of claim 23 wherein the first catalyst and the third catalyst are identical.
- 1 25. The method of claim 1 wherein a diol is produced in step (c), and wherein the solvent  
2 is capable of forming an azeotrope with the diol.
- 1 26. The method of claim 25 wherein the solvent comprises a halogenated aromatic  
2 hydrocarbon.
- 1 27. The method of claim 26 wherein the halogenated aromatic hydrocarbon is ortho-  
2 dichlorobenzene.

- 1 28. The method of claim 1 wherein step (c) comprises adding the solvent in an amount to  
2 produce a mixture containing from about 5% to about 25% solids by weight.
- 1 29. The method of claim 1 wherein the method further comprises adding water to the  
2 composition comprising the macrocyclic oligoester.
- 1 30. The method of claim 1 further comprising the step of:  
2 (d) separating the macrocyclic oligoester from the composition comprising the  
3 macrocyclic oligoester.
- 1 31. The method of claim 30 wherein step (d) comprises separating the macrocyclic  
2 oligoester by filtering.
- 1 32. The method of claim 31 wherein step (d) comprises separating the macrocyclic  
2 oligoester by filtering at a reduced temperature.
- 1 33. The method of claim 30 wherein step (d) comprises separating the macrocyclic  
2 oligoester by adsorption.
- 1 34. A method for preparing a macrocyclic oligoester comprising the steps of:  
2 (a) providing a composition comprising an intermediate molecular weight polyester;  
3 and  
4 (b) heating the composition comprising the intermediate molecular weight polyester in  
5 the presence of a catalyst and a solvent to produce a composition comprising the macrocyclic  
6 oligoester.
- 1 35. The method of claim 34 further comprising the step of:  
2 (c) separating the macrocyclic oligoester from the composition comprising the  
3 macrocyclic oligoester.
- 1 36. The method of claim 34 wherein the molecular weight of the intermediate molecular  
2 weight polyester is between about 20,000 Daltons and about 70,000 Daltons.
- 1 37. The method of claim 34 wherein step (b) comprises heating at a temperature between  
2 about 150°C and about 200°C.
- 1 38. The method of claim 34 wherein a diol is produced in step (b), and wherein the  
2 solvent is capable of forming an azeotrope with the diol.
- 1 39. The method of claim 34 wherein the solvent comprises a halogenated aromatic  
2 hydrocarbon.

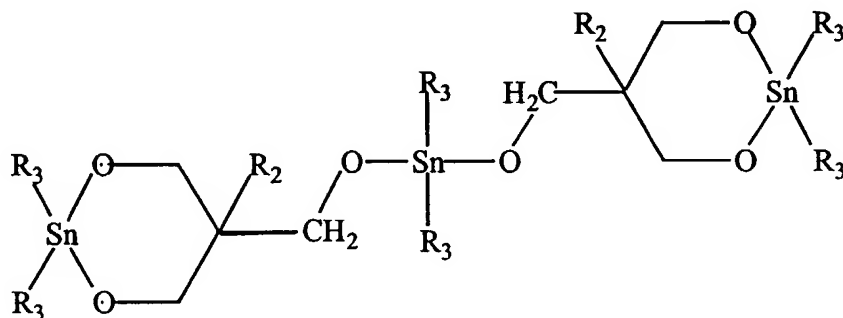


40. The method of claim 34 wherein step (b) comprises adding the solvent in an amount to produce a mixture containing from about 5% to about 25% solids by weight.

41. The method of claim 34 wherein the catalyst comprises a tin compound or a titanate compound.

42. The method of claim 41 wherein the tin compound comprises a compound selected from the group consisting of: (a) monoalkyltin(IV) hydroxide oxide, (b) monoalkyltin(IV) chloride dihydroxide, (c) dialkyltin(IV) oxide, (d) bistralkyltin(IV) oxide, (e) monoalkyltin(IV) trisalkoxide, (f) dialkyltin(IV) dialkoxide, (g) trialkyltin(IV) alkoxide, (h) a tin compound having the formula:

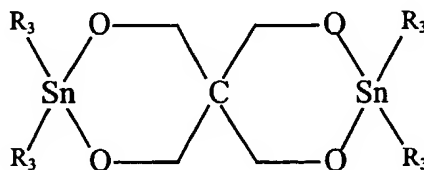
(III)



and

(i) a tin compound having the formula:

(IV)



wherein:

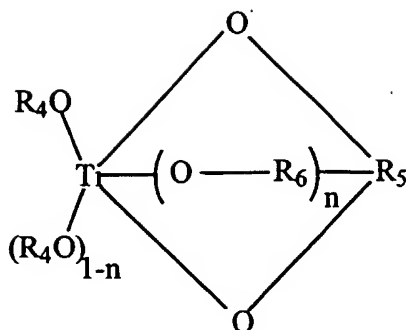
R<sub>2</sub> is a C<sub>1-4</sub> primary alkyl group, and

R<sub>3</sub> is C<sub>1-10</sub> alkyl group.

43. The method of claim 41 wherein the titanate compound comprises a compound selected from the group consisting of: (a) tetraisopropyl titanate, (b) isopropyl titanate, (c) tetraalkyl titanate, (d) titanate tetraalkoxide, (e) a titanate compound having the formula:

4

(V)



5

6

wherein:

7

each  $R_4$  is independently an alkyl group, or the two  $R_4$  groups taken together form a divalent aliphatic hydrocarbon group;

8

9

$R_5$  is a  $C_{2-10}$  divalent or trivalent aliphatic hydrocarbon group;

10

$R_6$  is a methylene or ethylene group; and

11

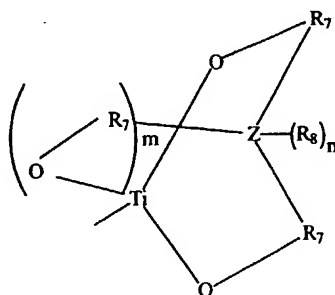
$n$  is 0 or 1,

12

(f) a titanate ester compound having at least one moiety of the formula:

13

(VI)



14

15

wherein:

16

each  $R_7$  is independently a  $C_{2-3}$  alkylene group;

17

$Z$  is O or N;

18

$R_8$  is a  $C_{1-6}$  alkyl group or unsubstituted or substituted phenyl group;

19

provided when  $Z$  is O,  $m=n=0$ , and when  $Z$  is N,  $m=0$  or 1 and  $m+n=1$ ,

20

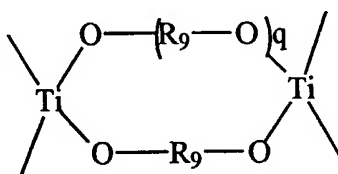
and

21

(g) a titanate ester compound having at least one moiety of the formula:

22

(VI)



23

24

wherein:

25 each R<sub>9</sub> is independently a C<sub>2-6</sub> alkylene group;

26 and q is 0 or 1.

44. A method for preparing a macrocyclic oligoester comprising the steps of:

(a) contacting a first compound having a structural formula:



wherein

R is an alkylene, a cycloalkylene, or a mono- or a polyoxyalkylene group;

with a second compound having a structural formula:



wherein

A is a divalent aromatic group or an alicyclic group, and

B is hydrogen or an alkyl group;

in the presence of a catalyst comprising a titanate compound at a temperature between about 140°C and about 200°C to produce a composition comprising a hydroxyalkyl-terminated polyester oligomer;

(b) heating the composition comprising the hydroxyalkyl-terminated polyester oligomer at a temperature between about 180°C and about 275°C and at a pressure between about 5 torr and about 625 torr to produce a composition comprising an intermediate molecular weight polyester, wherein the molecular weight of the intermediate molecular weight polyester is between about 20,000 Daltons and about 70,000 Daltons;

(c) heating the composition comprising the intermediate molecular weight polyester at a temperature between about 150°C and about 200°C in the presence of a solvent to produce a composition comprising a macrocyclic oligoester and a diol, wherein the solvent is capable of forming an azeotrope with the diol; and

(d) separating the macrocyclic oligoester from the composition comprising the macrocyclic oligoester.

## **METHODS FOR CONVERTING LINEAR POLYESTERS TO MACROCYCLIC OLIGOESTER COMPOSITIONS AND MACROCYCLIC OLIGOESTERS**

### **Abstract of the Disclosure**

Macrocyclic oligoesters and compositions comprising macrocyclic oligoesters are prepared from intermediate molecular weight polyesters. In one embodiment, a diol is contacted with a dicarboxylic acid or a dicarboxylate in the presence of a catalyst to produce a composition comprising a hydroxyalkyl-terminated polyester oligomer. The hydroxyalkyl-terminated polyester oligomer is heated to produce a composition comprising an intermediate molecular weight polyester which preferably has a molecular weight between about 20,000 Daltons and about 70,000 Daltons. The intermediate molecular weight polyester is heated and a solvent is added prior to or during the heating process to produce a composition comprising a macrocyclic oligoester. An optional step is to separate the macrocyclic oligoester from the composition comprising the macrocyclic oligoester.

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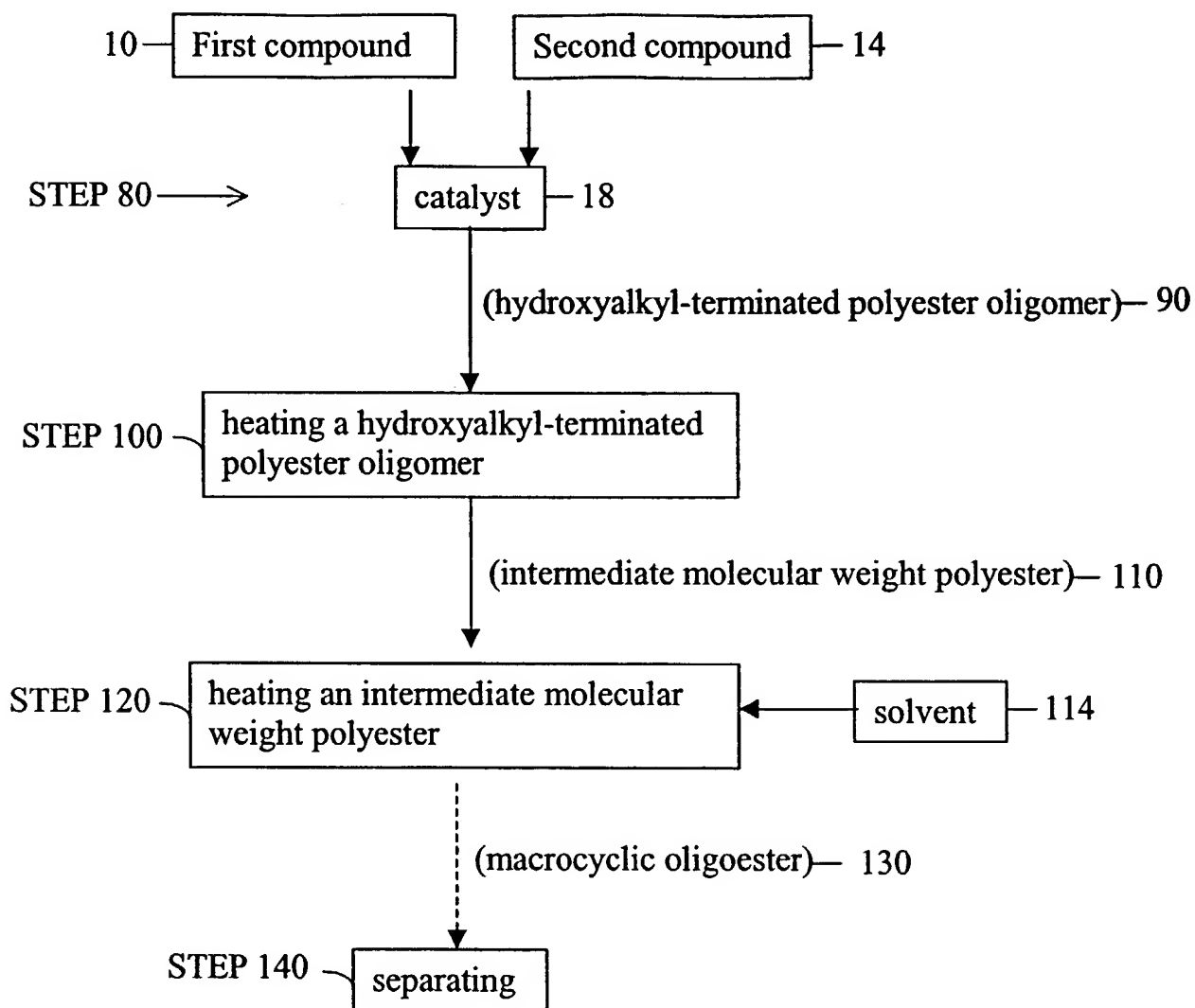


Figure 1

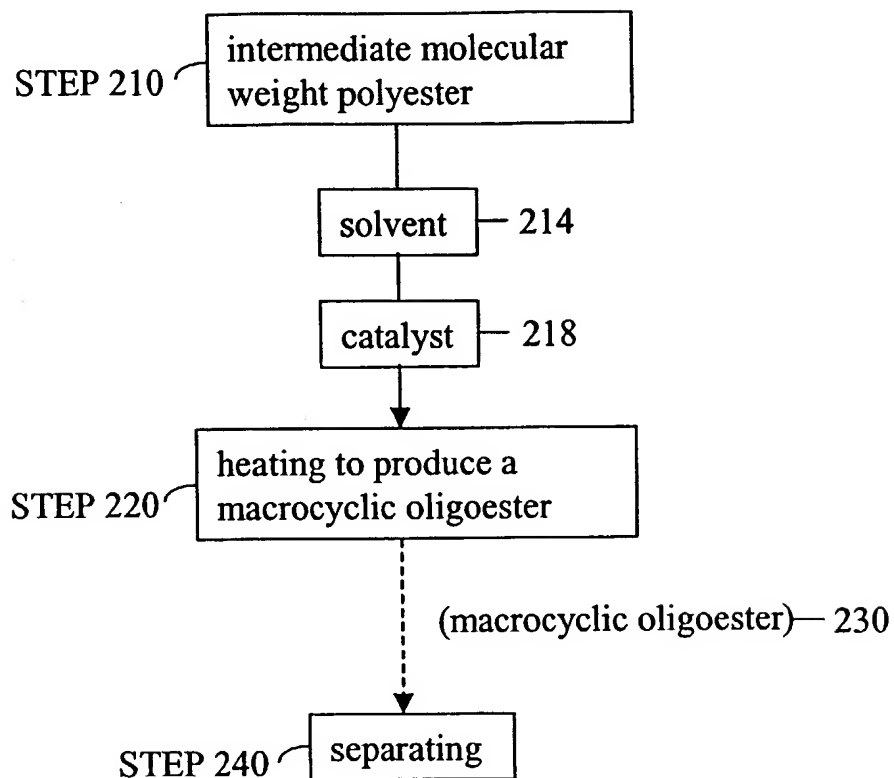


Figure 2



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APPLICATION NUMBER	FILING DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO.	DRAWINGS	TOT CLAIMS	IND CLAIMS
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## Applicant(s)

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Domestic Priority data as claimed by applicant

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## Title

Block copolymers from macrocyclic oligoesters and dihydroxyl-functionalized polymers

Preliminary Class

528

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BLOCK COPOLYMERS FROM MACROCYCLIC OLIGOESTERS AND  
DIHYDROXYL-FUNCTIONALIZED POLYMERS

Technical Field

[0001] This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to block copolymers and their preparation from macrocyclic oligoesters and dihydroxyl-functionalized polymers.

Background Information

[0002] Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss, and solvent resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding.

[0003] Recently, macrocyclic oligoesters were developed which are precursors to linear polyesters. Macrocyclic oligoesters exhibit low melt viscosity, which can be advantageous in some applications. Furthermore, certain macrocyclic oligoesters melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate catalyst, polymerization and crystallization can occur virtually isothermally.

[0004] Block copolymers such as copolyester elastomers are known that are typically prepared from short-chain aliphatic diols, aromatic diacids, and polyalkylene ether diols. For example, one commercial product is a copolymer of 1,4-butanediol, dimethyl terephthalate, and

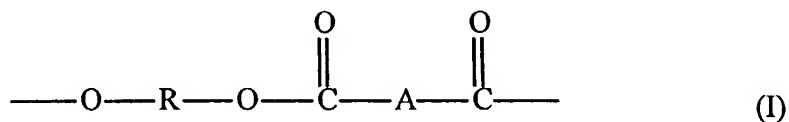


polytetramethylene ether glycol. This copolymer is prepared via polycondensation reactions in two steps at high temperature and high vacuum. The polycondensation reactions may take tens of hours or even days. In addition, the high temperature (about 250°C) that is necessary for the polycondensation reactions causes significant degradation of polytetramethylene ether glycol. Furthermore, the molecular weight of polytetramethylene ether glycol is limited to 1000 or less in order to minimize significant phase separation during the polycondensation reaction.

### Summary of the Invention

[0005] Block copolymers of high molecular weight have been prepared from macrocyclic oligoesters and dihydroxyl-functionalized polymers at an elevated temperature in the presence of a transesterification catalyst. The methods of the invention allow the design and control of the elasticity, the crystallinity, the ductility, and the molecular weight of the resulting block copolymers, while retaining other desirable properties of polyesters prepared from macrocyclic oligoesters as precursors.

[0006] In one aspect, the invention generally features a method for making a block copolymer. In one embodiment, the method includes the step of contacting a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst. The co-polymerization produces a block copolymer of polyester (derived from the macrocyclic oligoester) and the dihydroxyl-functionalized polymer. The macrocyclic oligoester has a structural repeat unit of formula (I):



wherein R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and A is a divalent aromatic or alicyclic group.

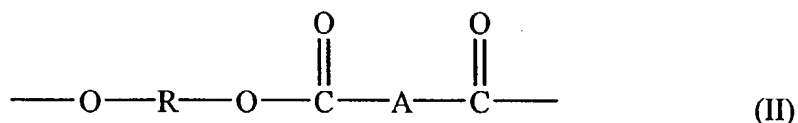
[0007] In another aspect, the invention features a method for making high molecular weight block copolymer. In one embodiment, the method includes the steps of: (a) contacting a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst to produce a block copolymer of polyester and the dihydroxyl-functionalized polymer; and (b) heating the block copolymer in the presence of a

chain extension agent. The chain extension step results in a higher molecular weight block copolymer of polyester and the dihydroxyl-functionalized polymer.

[0008] In yet another aspect, the invention features another method for making high molecular weight block copolymer. In one embodiment, the method includes the steps of (a) heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst, thereby producing a chain-extended dihydroxyl-functionalized polymer; and (b) contacting the chain-extended dihydroxyl-functionalized polymer with a macrocyclic oligoester at an elevated temperature in the presence of a transesterification catalyst. The co-polymerization produces a block copolymer of polyester and the chain-extended dihydroxyl-functionalized polymer.

[0009] In yet another aspect, the invention generally features a method for extending the chain length of a polyester polymer. In one embodiment, the method includes the step of contacting the polyester polymer and a chain extension agent at an elevated temperature.

[0010] In yet another aspect, the invention features a block copolymer. The block copolymer has at least two block units. The first block unit has, within its polymeric backbone, at least one first structural unit of formula (II)



where R is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group, and A is a divalent aromatic or alicyclic group. The second block unit has, within its polymeric backbone, at least one second structural unit of formula (III)



where B is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group. One or more of the carbon atoms in B may be replaced with an oxygen atom, a nitrogen atom, or a sulfur atom.

[0011] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following description and claims.

### Description

[0012] In an embodiment according to the present invention, high molecular weight block copolymers can be prepared from macrocyclic oligoesters and dihydroxyl-functionalized

polymers at an elevated temperature in the presence of a transesterification catalyst.

### **Definitions**

[0013] The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

[0014] As used herein, a "macrocyclic" molecule means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

[0015] As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

[0016] As used herein, an "oligoester" means a molecule that contains 2 or more identifiable ester functional repeat units of the same or different formula.

[0017] As used herein, a "macrocyclic oligoester" means a macrocyclic oligomer containing 2 or more identifiable ester functional repeat units of the same or different formula. A macrocyclic oligoester typically refers to multiple molecules of one specific formula having varying ring sizes. However, a macrocyclic oligoester may also include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. A macrocyclic oligoester may be a co-oligoester or multi-oligoester, i.e., an oligoester having two or more different structural repeat units having an ester functionality within one cyclic molecule.

[0018] As used herein, a "dihydroxyl-functionalized polymer" means a polymer having at least two hydroxyl functional groups. Typically, the at least two hydroxyl functional groups are at the ends of a polymer chain. However, the polymer may be branched and each of the two or more of branches of the polymer chain may have a hydroxyl functionalized end.

[0019] As used herein, "an alkylene group" means  $-C_nH_{2n}-$ , where  $n \geq 2$ .

[0020] As used herein, "a cycloalkylene group" means a cyclic alkylene group,  $-C_nH_{2n-x}-$ , where  $x$  represents the number of H's replaced by cyclization(s).

[0021] As used herein, "a mono- or polyoxyalkylene group" means  $[-(CH_2)_m-O-]_n-(CH_2)_m-$ , wherein  $m$  is an integer greater than 1 and  $n$  is an integer greater than 0.

[0022] As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

[0023] As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure therein.

[0024] As used herein, a "block copolymer" means a copolymer having segments of two or more polymers linked to one another. A block copolymer has constitutionally different structural units. Adjacent segments (i.e., blocks) contain structural units derived from different characteristic species of monomer or from structural repeat units with different composition or sequence distribution.

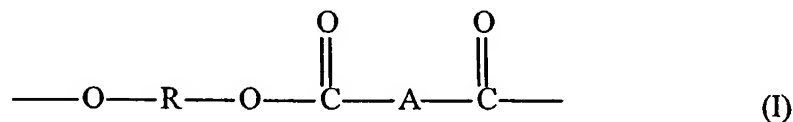
[0025] As used herein, a "chain extension agent" means an agent which facilitates extension of a polymer (or oligomer) chain.

[0026] As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as a fibrous or particulate material. Illustrative examples of particulate material are chopped fibers, glass microspheres, and crushed stone. Certain fillers and additives thus can be used to prepare polyester polymer composites. A fibrous material means a more continuous substrate, e.g., fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

### **Block Copolymers**

[0027] High molecular weight copolymers have been prepared from macrocyclic oligoesters and dihydroxyl-functionalized polymers at an elevated temperature in the presence of a transesterification catalyst.

[0028] In one aspect, the invention generally features a method for making a block copolymer. In one embodiment, the method includes the step of contacting a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst. The co-polymerization produces a block copolymer of polyester and the dihydroxyl-functionalized polymer. The macrocyclic oligoester has a structural repeat unit of formula (I):



wherein R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and A is a divalent aromatic or alicyclic group.

**[0029]** The co-polymerization reaction between a macrocyclic polyester oligomer and a dihydroxyl-functionalized polymer is typically completed within minutes. The duration of the co-polymerization reaction depends on many factors including the molar ratio of the macrocyclic oligoester to the di-hydroxyl-functionalized polymer, the molar ratio of the catalyst to the macrocyclic oligoester and the di-hydroxyl-functionalized polymer, the temperature at which the co-polymerization reaction is carried out, the desired molecular weight of the resulting block copolymer, and the choice of solvent and other reaction conditions. The co-polymerization reaction is preferably conducted under an inert environment, such as under nitrogen or argon, or under a vacuum.

**[0030]** The weight ratio of the dihydroxyl-functionalized polymer to macrocyclic oligoester can vary from about 0.01 to 10. In one embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 0.01 to about 0.1. In another embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 0.1 to about 1.0. In yet another embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 1.0 to about 5.0. In yet another embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 5.0 to about 10.

**[0031]** The molar ratio of the transesterification catalyst to the macrocyclic oligoester can range from about 0.01 to about 10 mole percent. In one embodiment, the molar ratio of the catalyst to the macrocyclic oligoester is from about 0.01 to about 0.1 mole percent. In another embodiment, the molar ratio of the catalyst to the macrocyclic oligoester is from about 0.1 to about 1 mole percent. In yet another embodiment, the molar ratio of the catalyst to the macrocyclic oligoester is from about 1 to about 10 mole percent.

**[0032]** The co-polymerization reaction between the macrocyclic oligoester and the dihydroxyl-functionalized polymer is carried out at an elevated temperature. In one embodiment, the temperature at which the co-polymerization is conducted ranges from about 130°C to about 300°C. In another embodiment, the temperature at which the co-polymerization is conducted ranges from about 130°C to about 300°C. In yet another embodiment, the temperature at which the co-polymerization is conducted ranges from about 150°C to about 260°C. In yet another embodiment, the temperature at which the co-polymerization is conducted ranges from about

170°C to about 210°C. In yet another embodiment, the temperature at which the co-polymerization is conducted ranges from about 180°C to about 190°C.

[0033] Yields of block copolymer depend on, among other factors, the precursor macrocyclic oligoester(s) used, the dihydroxyl-functionalized polymer(s) used, the polymerization catalyst(s) used, the reaction time, the reaction conditions, the presence or absence of chain-extension agent(s), and the work-up procedure. Typical yields range from about 90% to about 98% of the macrocyclic oligoester used. In one embodiment, the yield is within a range from about 92% to about 95%.

[0034] Block copolymers may be designed and prepared according to methods of the invention to achieve desired elasticity, crystallinity, and/or ductility. Block copolymers having a high weight percentage of the dihydroxyl-functionalized polymer content (e.g., polytetramethylene ether glycol), for example, exhibit an increased toughness and become elastomeric. Similar block copolymers having a low weight percentage of the dihydroxyl-functionalized polymer content exhibit an increased elasticity.

[0035] The co-polymerization reaction may be carried out with or without a solvent. A solvent may be used to dissolve one or more of the reactants and/or to mix the reactants. A solvent may also be used as a medium in which the reaction is carried out. Illustrative solvents that may be used include high-boiling compounds such as *o*-dichlorobenzene and meta-terphenyl. In another embodiment, no solvent is used in the co-polymerization reaction.

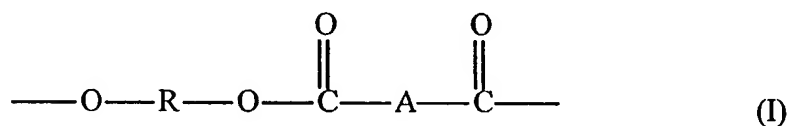
[0036] In one embodiment, the above method further includes a step of heating the block copolymer in the presence of a chain extension agent, thereby producing a block copolymer with a higher molecular weight. The chain extension agent may be any material that facilitates chain extension of the block copolymer including, for example, diacid chlorides, diisocyanates, and diepoxides. In one embodiment, 4,4'-methylenebis(phenyl isocyanate) is used as the chain extension agent. In another embodiment, terephthaloyl chloride is used as the chain extension agent. In yet another embodiment, a tin or a titanate compound is used as a chain extension agent. In yet another embodiment, two or more of these and other chain extension agents may be used together or sequentially.

[0037] The step of heating the block copolymer in the presence of a chain extension agent may be conducted at a temperature within a range from about 130°C to about 300°C. In one

embodiment, the step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 150°C to about 260°C. In another embodiment, the step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 170°C to about 210°C. In yet another embodiment, the step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 180°C to about 190°C.

[0038] One of the reactants employed in various embodiments of the invention to prepare block copolymers is a macrocyclic oligoester. Many different macrocyclic oligoesters readily can be made and are useful in the practice of this invention. Thus, depending on the desired properties of the final block copolymer product, the appropriate macrocyclic oligoester(s) can be selected for use in its manufacture.

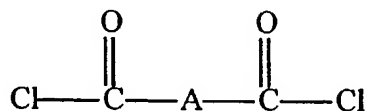
[0039] Macrocyclic oligoesters that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



wherein R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and A is a divalent aromatic or alicyclic group.

[0040] Preferred macrocyclic oligoesters are macrocyclic oligoesters of 1,4-butylene terephthalate, 1,3-propylene terephthalate, 1,4-cyclohexylenedimethylene terephthalate, ethylene terephthalate, and 1,2-ethylene 2,6-naphthalenedicarboxylate, and macrocyclic co-oligoesters comprising two or more of the above structural repeat units.

[0041] Synthesis of the macrocyclic oligoesters may be achieved by contacting at least one diol of the formula HO-R-OH with at least one diacid chloride of the formula:



where R and A are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An

illustrative example of such amines is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is within the range of from about  $-25^{\circ}\text{C}$  to about  $25^{\circ}\text{C}$ . See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

[0042] Macrocyclic oligoesters also can be prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as triethylamine. The condensation reaction is conducted in a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

[0043] Another method for preparing macrocyclic oligoesters or macrocyclic co-oligoesters is the depolymerization of linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to macrocyclic oligoesters by heating a mixture of linear polyesters, an organic solvent, and a transesterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

[0044] It is also within the scope of the invention to employ macrocyclic co-oligoesters to produce block copolymers. Therefore, unless otherwise stated, an embodiment of a composition, article, or methods that refers to macrocyclic oligoesters also includes embodiments utilizing macrocyclic co-oligoesters.

[0045] Dihydroxyl-functionalized polymers employed in various embodiments of the invention include any dihydroxyl-functionalized polymer that reacts with a macrocyclic oligoester to form a block copolymer under transesterification conditions. Illustrative examples of classes of dihydroxyl-functionalized polymers include polyethylene ether glycols, polypropylene ether glycols, polytetramethylene ether glycols, polyolefin diols, polycaprolactone diols, polyperfluoroether diols, and polysiloxane diols. Illustrative examples of dihydroxyl-functionalized polymers include dihydroxyl-functionalized polyethylene terephthalate and dihydroxyl-functionalized polybutylene terephthalate. The molecular weight of the dihydroxyl-

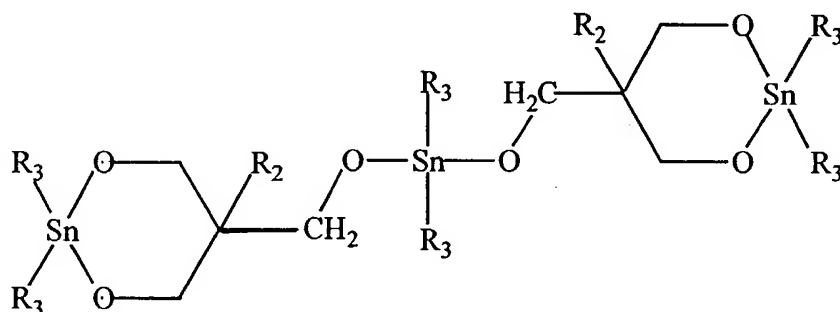


functionalized polymer used may be, but is not limited to, about 500 to about 100,000. In one embodiment, the molecular weight of the dihydroxyl-functionalized polymer used is within a range from about 500 to about 50,000. In another embodiment, the molecular weight of the dihydroxyl-functionalized polymer used is within a range from about 500 to about 10,000.

[0046] Catalysts employed in the invention are those that are capable of catalyzing a transesterification polymerization of a macrocyclic oligoester with a dihydroxyl-functionalized polymer. One or more catalysts may be used together or sequentially. As with state-of-the-art processes for polymerizing macrocyclic oligoesters, organotin and organotitanate compounds are the preferred catalysts, although other catalysts may be used.

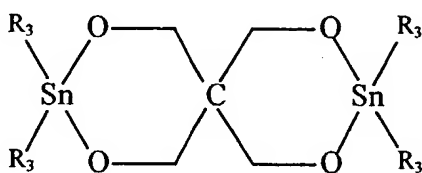
[0047] Illustrative examples of classes of tin compounds that may be used in the invention include monoalkyltin(IV) hydroxide oxides, monoalkyltin(IV) chloride dihydroxides, dialkyltin(IV) oxides, bistralkyltin(IV) oxides, monoalkyltin(IV) trisalkoxides, dialkyltin(IV) dialkoxides, trialkyltin(IV) alkoxides, tin compounds having the formula (IV):

(IV)



and tin compounds having the formula (V):

(V)



wherein  $R_2$  is a  $C_{1-4}$  primary alkyl group, and  $R_3$  is  $C_{1-10}$  alkyl group.

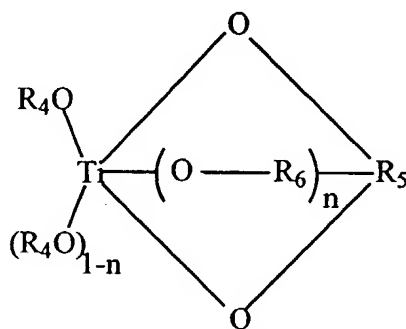
[0048] Specific examples of organotin compounds that may be used in this invention include dibutyltin dioxide, 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane, n-butyltin(IV) chloride dihydroxide, di-n-butyltin(IV) oxide, dibutyltin dioxide, di-n-octyltin oxide,

n-butyltin tri-n-butoxide, di-n-butyltin(IV) di-n-butoxide, 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.* In addition, tin catalysts described in commonly owned U.S.S.N. 09/754,943 (incorporated by reference below) may be used in the polymerization reaction.

[0049] Titanate compounds that may be used in the invention include titanate compounds described in commonly owned U.S.S.N. 09/754,943 (incorporated by reference below).

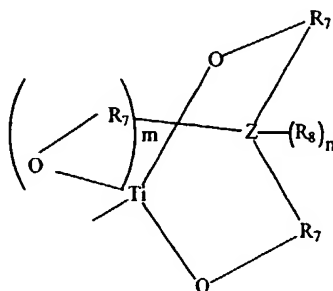
Illustrative examples include tetraalkyl titanates (e.g., tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, and tetrabutyl titanate), isopropyl titanate, titanate tetraalkoxide. Other illustrative examples include (a) titanate compounds having the formula (VI):

(VI)



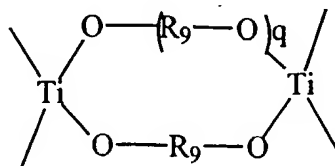
wherein each  $R_4$  is independently an alkyl group, or the two  $R_4$  groups taken together form a divalent aliphatic hydrocarbon group;  $R_5$  is a  $C_{2-10}$  divalent or trivalent aliphatic hydrocarbon group;  $R_6$  is a methylene or ethylene group; and  $n$  is 0 or 1, (b) titanate ester compounds having at least one moiety of the formula (VII):

(VII)



wherein each  $R_7$  is independently a  $C_{2-3}$  alkylene group;  $Z$  is O or N;  $R_8$  is a  $C_{1-6}$  alkyl group or unsubstituted or substituted phenyl group; provided when  $Z$  is O,  $m=n=0$ , and when  $Z$  is N,  $m=0$  or 1 and  $m+n=1$ , and (c) titanate ester compounds having at least one moiety of the formula (VIII):

(VIII)



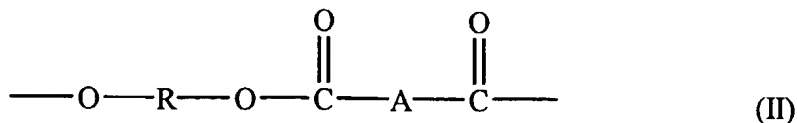
wherein each R<sub>9</sub> is independently a C<sub>2-6</sub> alkylene group; and q is 0 or 1.

**[0050]** The resulting high molecular weight block copolymer of polyester and the dihydroxyl-functionalized polymer may have a molecular weight within a range from about 10,000 to 300,000. In one embodiment, the molecular weight of the block copolymer of polyester and the dihydroxyl-functionalized polymer is within a range from about 10,000 to about 70,000. In another embodiment, the molecular weight of the block copolymer of polyester and the dihydroxyl-functionalized polymer is within a range from about 70,000 to about 150,000. In yet another embodiment, the molecular weight of the block copolymer of polyester and the dihydroxyl-functionalized polymer is within a range from about 150,000 to about 300,000.

**[0051]** In another aspect, the invention relates to a method for making high molecular weight block copolymer comprising the steps of contacting a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst to produce a block copolymer of polyester and the dihydroxyl-functionalized polymer; and heating the block copolymer in the presence of a chain extension agent, thereby producing a high molecular weight block copolymer of polyester and the dihydroxyl-functionalized polymer.

**[0052]** In one embodiment, a high molecular weight block copolymer is produced after heating the block copolymer of polyester and the dihydroxyl-functionalized polymer produced in the first step in the presence of a chain extension agent. The step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 130°C to about 300°C. In one embodiment, the step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 150°C to about 260°C. In another embodiment, the step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 170°C to about 210°C. In yet another embodiment, the step of heating the block copolymer in the presence of a chain extension agent is conducted at a temperature within a range from about 180°C to about 190°C.

[0053] In yet another aspect, the invention features a block copolymer. The block copolymer contains at least a first block unit and a second block unit. The first block unit has, within its polymeric backbone, at least one structural unit of formula (II)



where R is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group, and A is a divalent aromatic or alicyclic group. The second block unit has, within its polymeric backbone, at least one second structural unit of formula (III)



where B is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group, one or more of the carbon atoms in B may be replaced with an oxygen atom, a nitrogen atom, or a sulfur atom.

[0054] Illustrative examples of block unit B include a polyethylene ether group, a polypropylene ether group, a polymethylene ether group, a polyolefin group, a polycaprolactone group, a polyperfluoroether diol, and a polysiloxane diol.

[0055] The block copolymer prepared from a macrocyclic oligoester and a di-hydroxyl-functionalized polymer may contain blocks derived from the macrocyclic oligoester, blocks derived from the dihydroxyl-functionalized polymer, and blocks derived from both the macrocyclic oligoester and the dihydroxyl-functionalized polymer. The length of the individual blocks and the sequence thereof can be designed to serve particular applications.

[0056] In another aspect, the invention features a method for making high molecular weight block copolymer. In one embodiment, the method includes the steps of: (a) heating a dihydroxyl-functionalized polymer and a diester in the presence of a chain extension agent, thereby producing a chain-extended dihydroxyl-functionalized polymer; and (b) contacting the chain-extended dihydroxyl-functionalized polymer and a macrocyclic oligoester at an elevated temperature in the presence of a transesterification catalyst. The co-polymerization produces a block copolymer of polyester and the chain-extended dihydroxyl-functionalized polymer.

[0057] The diester that may be employed include dialkyl terephthalates such as dimethyl terephthalate and dimethyladipate.

[0058] The step of heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst may be conducted at a temperature within a range from about

130°C to about 300°C. In one embodiment, the step of heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst is conducted at a temperature within a range from about 150°C to about 260°C. In another embodiment, the step of heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst is conducted at a temperature within a range from about 170°C to about 210°C. In yet another embodiment, the step of heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst is conducted at a temperature within a range from about 180°C to about 190°C.

[0059] The amount of the diester used depends on factors including the desired molecular weight of the block copolymer to be produced. In one embodiment, the molar ratio of the diester to the dihydroxyl-functionalized polymer is within a range from about 0.1000 to about 0.9999.

[0060] The step of heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst may be conducted under a vacuum. It may also be conducted in an inert environment such as argon or nitrogen. The reaction is completed within about 5 minutes to about 45 minutes, and typically within about 30 minutes.

[0061] In another aspect, the invention features a method for extending the chain length of a polyester polymer. In one embodiment, the method includes the step of contacting the polyester polymer and a chain extension agent at an elevated temperature. The polyester polymer may be any polyester polymer including polybutylene terephthalate and polyethylene terephthalate.

[0062] The compositions and methods of the invention may be used to manufacture articles of various size and shape from various macrocyclic oligoesters and dihydroxyl-functionalized polymers. Exemplary articles that may be manufactured by the invention include without limitation automotive body panels and chassis components, bumper beams, aircraft wing skins, windmill blades, fluid storage tanks, tractor fenders, tennis rackets, golf shafts, windsurfing masts, toys, rods, tubes, bars stock, bicycle forks, and machine housings.

[0063] In the manufacture of an article, various types of fillers may be included. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester polymer product. A filler also may provide or reduce color,

provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silicate, titanium dioxide, calcium carbonate, chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers. Fillers can be used to prepare polyester polymer composites.

[0064] Furthermore, in the manufacture of an article additional components (e.g., additives) may be added. Illustrative additives include colorants, pigments, magnetic materials, anti-oxidants, UV stabilizers, plasticizers, fire-retardants, lubricants, and mold releases.

### **Examples**

[0065] The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention. The products obtained from these examples may be confirmed by conventional techniques such as proton and carbon-13 nuclear magnetic resonance spectroscopy, mass spectroscopy, infrared spectroscopy, differential scanning calorimetry and gel permeation chromatography analyses.

#### ***Example A***

[0066] The macrocyclic oligoesters employed was a mixture of oligomers having various degrees of polymerization with 95 mole percent 1,4-butylene terephthalate units and 5 mole percent ethylene terephthalate units. The macrocyclic oligoesters were prepared by heating a mixture of polyester linears, organic solvents, such as *o*-xylene and *o*-dichlorobenzene, which are substantially free of oxygen and water, and tin or titanium compounds as transesterification catalysts. See U.S. Patent No. 5,668,186 (incorporated herein by reference in its entirety).

#### ***Example 1***

[0067] A small vial (21x70mm, 4 dram) equipped with a magnetic stir and a nitrogen/vacuum adaptor, was charged with 2.0 grams (8.91 mmol based on structural units) of the macrocyclic (1,4-butylene terephthalate) oligoester and pre-determined amount of dihydroxyl terminated polymer. The mixture was dried by heating at about 190°C/1 torr for 5 minutes. The vacuum

was released with nitrogen. A polymerization catalyst (0.30 mole percentage) was added as a solution in *o*-dichlorobenzene. The reaction time was measured from the time of catalyst addition. The time for the melt to stop the magnetic stirrer was noted as the end of the induction period. After the magnetic stirrer stopped, heating was continued under nitrogen for about 15 to 30 minutes during which time crystallization of the polymerized product began to yield white solid. At the end of the polymerization, the vial was cooled to room temperature and was broken to remove the polymer product. The polymer product was analyzed by gel permeation chromatography to determined percent polymerization and molecular weight relative to polystyrene. The results are shown in Table 1.

**Table 1. Co-polymerization of Macrocyclic Oligoesters with Dihydroxyl-Functionalized Polymer at 190°C**

Dihydroxyl-terminated polymer	Catalyst used	Dihydroxyl-terminated polymer, wt%	Induction Period, seconds <sup>a</sup>	Polymerization Time, minutes	Polymer Yield, %	Mw of Polymer
poly(ethylene-co-1,2-butylene) diol <sup>b</sup>	stannoxane <sup>c</sup>	10	30	15	97	74,000
Terathane 2900 <sup>d</sup>	stannoxane <sup>c</sup>	5	30	15	96	105,000
Terathane 2900 <sup>d</sup>	stannoxane <sup>c</sup>	10	35	15	98	60,000
Terathane 2900 <sup>d</sup>	stannoxane <sup>c</sup>	20	20	15	95	45,000
Terathane 2900 <sup>d</sup>	stannoxane <sup>c</sup>	40	90	15	94	26,000
Terathane 2900 <sup>d</sup>	stannoxane <sup>c</sup>	60	95	15	96	17,000
Terathane 2900 <sup>d</sup>	dibutyltin dibutoxide	60	90	15	98	30,000
poly(butadiene) diol <sup>e</sup>	dibutyltin dibutoxide	30	90	30	insoluble gel	insoluble gel

- a) Time required to stop the magnetic stirrer
- b) Poly(ethylene-1,2-butylene) diol, Mw of 3,400
- c) 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane
- d) Polytetramethylene ether glycol, Mw = 2,900 (trade name Hytrel, available from E.I. du Pont Nemours and Company, Wilmington, Delaware)
- e) Poly(butadiene) diol, Mw of 2,800

### Example 2

[0068] To a 50 ml one-neck round-bottom flask equipped with a magnetic stir, a dean-stark trap, and a condenser, 2.4 grams (10.91 mmol ester groups) of macrocyclic (1,4-butylene

terephthalate) oligoester, 3.6 grams (2.48 mmol hydroxyl groups) of polytetramethylene ether glycol Terathane 2900 and 15 ml of *o*-dichlorobenzene were added. The mixture was heated to reflux in an oil bath at about 190°C. After removal of 3 ml of *o*-dichlorobenzene, an *o*-dichlorobenzene solution of tin catalyst Fomrez SUL-11A, which is a 1:1 reaction mixture of dibutyltin dioxide/DIOP plasticizer from Witco Chemicals (Crompton Corporation), was added to yield 0.3 mole % tin based on ester groups. The mixture was heated under reflux in nitrogen atmosphere for about 90 minutes. Then, 1.5 mmol of 4,4'-methylenebis(phenyl isocyanate) was added. Significant increase in viscosity was observed immediately. The mixture was heated for another 5 minutes and was cooled to room temperature. The viscous solution was then diluted with *o*-dichlorobenzene and was added to 100 ml of heptane. The resulting polymer precipitated out of the solution. After filtration, the resulting fibrous polymer product was dried overnight at about 80°C under vacuum. The polymer product was analyzed by gel permeation chromatography to determined percent polymerization and molecular weight relative to polystyrene. The results are shown in Table 2.

**Table 2. Co-polymerization of Macrocyclic Oligoesters and Dihydroxyl-Functionalized Polymer with 4,4'-methylenebis(phenyl isocyanate) as chain-extension Agent**

Terathane 2900, wt%	Polymerization Time, minutes	Polymer Yield, %	Mw of Polymer
40	90	97	85,300
20	90	97	120,300
70	90	96	141,200
50	90	96	128,100
poly(ethylene-co-1,2-butylene) diol; 50%	90	95	131,700

**Example 3**

[0069] To a small vial (21x70 mm, 4 dram) equipped with a magnetic stir and a nitrogen/vacuum adaptor, 4.0 grams of polyteramethylene ether glycol Terathane 2900, 0.214 gram (1.10 mmol) of dimethyl terephthalate and 2.8 mg (0.011 mmol) of monobutyltin chloride dihydroxide were added. The mixture was heated under vacuum to 190°C for 30 minutes. Then, 2.67 grams (12.14 mmol) of macrocyclic (1,4-butylene terephthalate) oligoester was added to the



viscous liquid mixture. The mixture was heated at about 190°C under nitrogen for about 60 minutes during which time crystallization of the polymerized product began to yield a white solid. At the end of the polymerization, the vial was cooled to room temperature and was broken to remove the polymer product. The polymer product was analyzed by gel permeation chromatography to determined percent polymerization and molecular weight relative to polystyrene. The results are shown in Table 3.

**Table 3. Co-polymerization of Macrocyclic Oligoesters and Dihydroxyl-Functionalized Polymer and Dimethyl Terephthalate**

<b>Terathane 2900, wt%</b>	<b>Polymerization Time, minutes</b>	<b>Polymer Yield, %</b>	<b>Mw of Polymer</b>	<b>T<sub>m</sub><sup>a</sup> (°C)</b>	<b>ΔH<sup>b</sup> (J/g)</b>
40	60	97	90,000	213	25
60	60	96	85,000	210	22
70	60	95	80,000	207	15

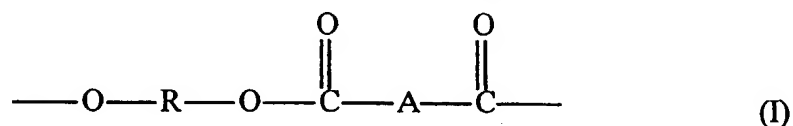
- a) Peak temperature of the melting endotherm determined by DSC with a heating rate of 20°C/min
- b) Heat of melting determined by DSC with a heating rate of 20°C/min

[0070] Each of the patent documents disclosed hereinabove is incorporated by reference herein in their entirety. Variations, modifications, and other implementations of what is described herein will occur to those of ordinary skill in the art without departing from the spirit and the scope of the invention as claimed. Accordingly, the invention is to be defined not by the preceding illustrative description but instead by the spirit and scope of the following claims.

## CLAIMS

What is claimed is:

1. A method for making a block copolymer, the method comprising the step of contacting a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst, thereby producing the block copolymer of polyester and the dihydroxyl-functionalized polymer, wherein the macrocyclic oligoester has a structural repeat unit of formula (I):

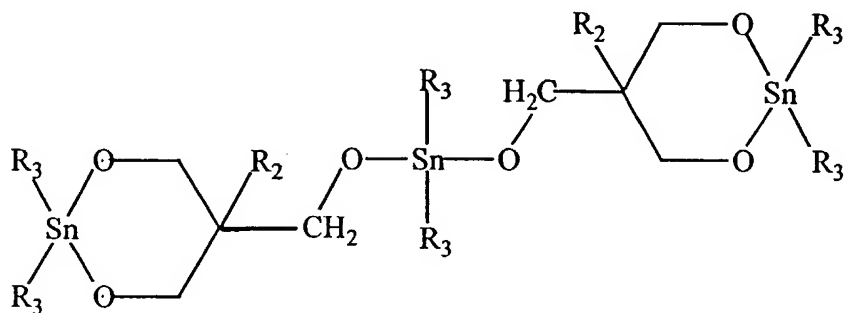


wherein R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and A is a divalent aromatic or alicyclic group.

2. The method of claim 1 wherein the macrocyclic oligoester comprises at least one of a macrocyclic oligo(1,4-butylene terephthalate) and a macrocyclic oligo(ethylene terephthalate).
3. The method of claim 1 wherein the dihydroxyl-functionalized polymer comprises at least one of a polyethylene ether glycol, a polypropylene ether glycol, a polytetramethylene ether glycol, a polyolefin diol, a polycaprolactone diol, a polyperfluoroether diol, and a polysiloxane diol.
4. The method of claim 1 wherein the dihydroxyl-functionalized polymer comprises at least one of a dihydroxyl-functionalized polyethylene terephthalate and a dihydroxyl-functionalized polybutylene terephthalate.
5. The method of claim 1 wherein the dihydroxyl-functionalized polymer has a molecular weight in a range from about 500 to about 100,000.
6. The method of claim 5 wherein the dihydroxyl-functionalized polymer has a molecular weight in a range from about 500 to about 10,000.
7. The method of claim 1 wherein the weight ratio of the dihydroxyl-functionalized polymer to the macrocyclic oligoester is in a range from about 0.01 to about 10.0.

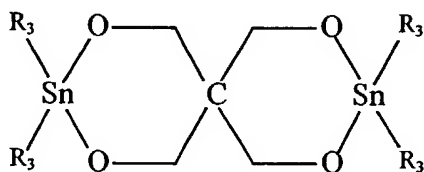
8. The method of claim 7 wherein the weight ratio of the dihydroxyl-functionalized polymer to the macrocyclic oligoester is in a range from about 0.1 to about 3.0.
9. The method of claim 1 wherein the molecular weight of the block copolymer is in a range from about 10,000 to about 300,000.
10. The method of claim 9 wherein the molecular weight of the block copolymer is in a range from about 40,000 to about 160,000.
11. The method of claim 1 wherein the transesterification catalyst is present in an amount from about 0.01 to about 10 mole percent of the macrocyclic oligoester.
12. The method of claim 1 wherein the transesterification catalyst comprises a tin compound.
13. The method of claim 12 wherein the tin compound comprises at least one of a monoalkyltin(IV) hydroxide oxide, a monoalkyltin(IV) chloride dihydroxide, a dialkyltin(IV) oxide, a bistralkyltin(IV) oxide, a monoalkyltin(IV) trisalkoxide, a dialkyltin(IV) dialkoxide, a trialkyltin(IV) alkoxide, a tin compound having the formula (IV):

(IV)



and a tin compound having the formula (V):

(V)



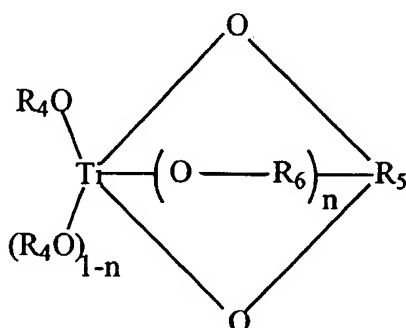
wherein:

$R_2$  is a  $C_{1-4}$  primary alkyl group, and

$R_3$  is  $C_{1-10}$  alkyl group.

14. The method of claim 12 wherein the tin compound comprises at least one of 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane, dibutyltin dibutoxide, dibutyltin dioxide, and monobutyltin chloride dihydroxide.
15. The method of claim 1 wherein the transesterification catalyst comprises a titanate compound.
16. The method of claim 15 wherein the titanate compound comprises at least one of (a) tetraisopropyl titanate, (b) isopropyl titanate, (c) tetraalkyl titanate, (d) titanate tetraalkoxide, (e) a titanate compound having the formula (VI):

(VI)



wherein:

each  $R_4$  is independently an alkyl group, or the two  $R_4$  groups taken together form a divalent aliphatic hydrocarbon group;

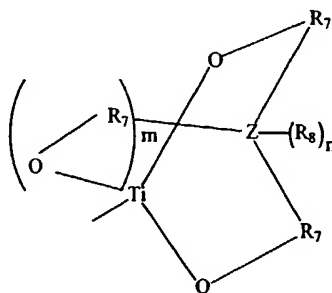
$R_5$  is a  $C_{2-10}$  divalent or trivalent aliphatic hydrocarbon group;

$R_6$  is a methylene or ethylene group; and

$n$  is 0 or 1,

(f) a titanate ester compound having at least one moiety of the formula (VII):

(VII)



wherein:

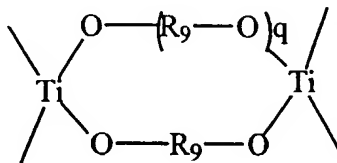
each  $R_7$  is independently a  $C_{2-3}$  alkylene group;

Z is O or N;

R<sub>8</sub> is a C<sub>1-6</sub> alkyl group or unsubstituted or substituted phenyl group;

provided when Z is O, m=n=0, and when Z is N, m=0 or 1 and m+n = 1,

and (g) a titanate ester compound having at least one moiety of the formula (VIII):  
(VIII)



wherein:

each R<sub>9</sub> is independently a C<sub>2-6</sub> alkylene group;

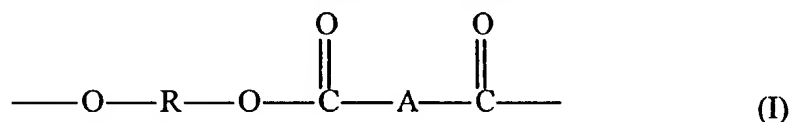
and q is 0 or 1.

17. The method of claim 1 wherein the elevated temperature is within a temperature range from about 130°C to about 300°C.
18. The method of claim 17 wherein the elevated temperature is within a temperature range from about 150°C to about 260°C.
19. The method of claim 18 wherein the elevated temperature is within a temperature range from about 170°C to about 210°C.
20. The method of claim 1 further comprising the step of heating the block copolymer in the presence of a chain extension agent.
21. The method of claim 20 wherein the chain extension agent comprises at least one of a diacid chloride, a diisocyanate, and a diepoxide.
22. The method of claim 21 wherein the chain extension agent comprises at least one of 4,4'-methylenebis(phenyl isocyanate) and terephthaloyl chloride.
23. A block copolymer prepared by the method of claim 1.
24. A composite material comprising the block copolymer prepared by the method of claim 1.
25. An article of manufacture comprising the block copolymer prepared by the method of claim 1.
26. The method of claim 1 further comprising the step of heating the dihydroxyl-functionalized polymer with a diester at a temperature range from about 130°C to about 300°C in the presence of a transesterification catalyst before the step of contacting a

macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst.

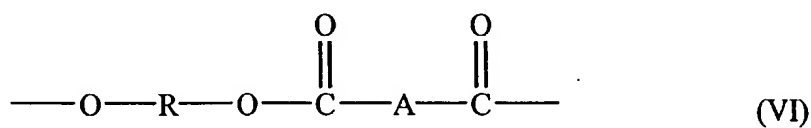
27. The method of claim 26 wherein the diester comprises a dimethyl terephthalate.
28. The method of claim 26 wherein the temperature range is from about 150°C to about 260°C.
29. The method of claim 28 wherein the temperature range is from about 170°C to about 210°C.
30. A method for making high molecular weight block copolymer comprising the steps of:
  - (a) contacting a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a transesterification catalyst to produce the block copolymer of polyester and the dihydroxyl-functionalized polymer; and
  - (b) heating the block copolymer in the presence of a chain extension agent, thereby producing a high molecular weight block copolymer of polyester and the dihydroxyl-functionalized polymer,

wherein the macrocyclic oligoester has a structural repeat unit of formula (I):



wherein R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and A is a divalent aromatic or alicyclic group.

31. The method of claim 30 wherein step (b) comprises heating at a temperature range from about 130°C to about 300°C.
32. The method of claim 30 wherein step (b) comprises heating at a temperature range from about 150°C to about 260°C.
33. The method of claim 30 wherein step (b) comprises heating at a temperature range from about 170°C to about 210°C.
34. A block copolymer comprising a first block unit comprising, within its polymeric backbone, at least one first structural unit of formula (VI)



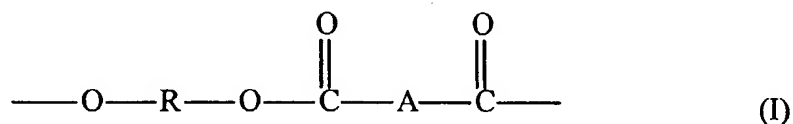
where R is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group, and A is a divalent aromatic or alicyclic group;  
and a second block unit comprising, within its polymeric backbone, at least one second structural unit of formula (VII)



where B is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group, one or more of the carbon atoms in B may be replaced with an oxygen atom, a nitrogen atom, or a sulfur atom.

35. The block copolymer of claim 34 wherein B comprises at least one of a polyethylene ether group, a polypropylene ether group, a polymethylene ether group, a polyolefin group, a polycaprolactone group, a polyperfluoroether diol, and a polysiloxane diol.
36. A composite material comprising the block copolymer of claim 34.
37. An article of manufacture comprising the block polymer of claim 34.
38. The block copolymer of claim 34 having a molecular weight of from about 10,000 to about 300,000.
39. A method for making high molecular weight block copolymer comprising the steps of:
  - (a) heating a dihydroxyl-functionalized polymer with a diester in the presence of a transesterification catalyst thereby producing a chain-extended dihydroxyl-functionalized polymer; and
  - (b) contacting the chain-extended dihydroxyl-functionalized polymer with a macrocyclic oligoester at an elevated temperature in the presence of a transesterification catalyst, thereby producing a block copolymer of polyester and the chain-extended dihydroxyl-functionalized polymer,

wherein the macrocyclic oligoester has a structural repeat unit of formula (I):



wherein R is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and A is a divalent aromatic or alicyclic group.

40. The method of claim 39 wherein the diester comprises dimethyl terephthalate.

41. The method of claim 40 wherein step (a) comprises heating at a temperature range from about 130°C to about 300°C.
42. The method of claim 41 wherein step (a) comprises heating at a temperature range from about 150°C to about 260°C.
43. The method of claim 39 wherein step (a) comprises heating at a temperature range from about 170°C to about 210°C.
44. A method for extending the chain length of a polyester polymer comprising the step of contacting the polyester polymer and a chain extension agent at an elevated temperature.
45. The method of claim 44 wherein the chain extension agent comprises at least one of a diacid chloride, a diisocyanate, and a diepoxide.
46. The method of claim 45 wherein the chain extension agent comprises at least one of 4,4'-methylenebis(phenyl isocyanate) and terephthaloyl chloride.
47. The method of claim 44 wherein the polyester polymer comprises a copolymer of a macrocyclic oligoester and a dihydroxyl-functionalized polymer.



BLOCK COPOLYMERS FROM MACROCYCLIC OLIGOESTERS AND  
DIHYDROXYL-FUNCTIONALIZED POLYMERS

Abstract of the Disclosure

Block copolymers are prepared from polymerization of a macrocyclic oligoester and a dihydroxyl-functionalized polymer at an elevated temperature in the presence of a polymerization catalyst.

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## Title

High molecular weight copolyesters from macrocyclic oligoesters and cyclic esters

Preliminary Class

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Data entry by : DUONG, SANG

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HIGH MOLECULAR WEIGHT COPOLYESTERS FROM MACROCYCLIC  
OLIGOESTERS AND CYCLIC ESTERS

Technical Field

[0001] This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to high molecular weight copolyesters and their preparation from macrocyclic oligoesters and cyclic esters.

Background Information

[0002] Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss and solvent resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding.

[0003] Recently, macrocyclic oligoesters were developed which have unique properties. These properties make them attractive as matrices for engineering thermoplastic composites. The desirable properties stem from the fact that macrocyclic oligoesters exhibit low melt viscosity, allowing them easily to impregnate a dense fibrous preform followed by polymerization to polyesters. Furthermore, certain macrocyclic oligoesters melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate catalyst, polymerization and crystallization can occur virtually isothermally.

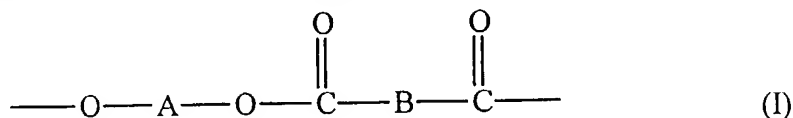
[0004] Despite the above-described properties and other advantages, some of the resulting polyesters prepared from macrocyclic oligoesters typically display an increase in crystallinity that

invariably diminishes the favorable properties including the polymer's ductility. Thus, methods are needed for preparing polyesters with favorable crystallinity and ductility while retaining the advantages of using macrocyclic oligoesters as precursors to polyesters.

### Summary of the Invention

[0005] Copolyesters of high molecular weight have been prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst. The copolyesters so prepared show favorable crystallinity and ductility while retaining other desirable properties of polyesters prepared from macrocyclic oligoesters as precursors.

[0006] In one aspect, the invention generally features a method of making a copolyester. In one embodiment, the method includes the steps of providing a macrocyclic oligoester, providing a cyclic ester other than a macrocyclic oligoester, and contacting the macrocyclic oligoester and the cyclic ester in the presence of a transesterification catalyst at an elevated temperature to produce a copolyester. The macrocyclic oligoester has a structural repeat unit of formula (I):



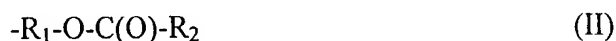
wherein A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group.

[0007] In another aspect, the invention generally features a method of making a block copolymer of polyesters. In one embodiment, the method includes contacting a macrocyclic oligoester and a transesterification catalyst at an elevated temperature to form a first polymeric segment. Subsequently contacting the first polymeric segment, a cyclic ester that is not a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps then are sequentially repeated a desired number of times to form a block copolyester having additional first and second polymeric segments.

[0008] In another embodiment that is a variation of the above method of making a block copolymer, a first polymeric segment is formed by contacting a cyclic ester that is not a macrocyclic oligoester and a transesterification catalyst at an elevated temperature. Subsequently contacting this first polymeric segment, a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps then are

sequentially repeated a desired number of times to form a block copolymer having additional first and second polymeric segments.

[0009] In yet another aspect, the invention features a composition that is a copolyester. In one embodiment, the copolyester contains, within its polymeric backbone, at least one structural unit of formula (I) (as defined above) and at least one structural unit of formula (II)



wherein  $R_1$  and  $R_2$  are independently an organic moiety with the proviso that  $R_1$  is not  $-O-A'$  if  $R_2$  is  $-B'-C(O)-$ .  $A'$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group.  $B'$  is a divalent aromatic or alicyclic group.

[0010] In yet another aspect, the invention features a block copolymer of polyesters. A first block unit of the copolymer has, within its polymeric backbone, at least one first structural unit of formula (I), as defined above. A second block unit has, within its polymeric backbone, at least one second structural unit of formula (II), as defined above.

[0011] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following description and claims.

#### Description

[0012] The present invention is related to the surprising discovery that high molecular weight copolyesters having favorable crystallinity and ductility can be prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst.

#### Definitions

[0013] The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

[0014] As used herein, a "macrocyclic" molecule means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

[0015] As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

[0016] As used herein, an "oligoester" means a molecule that contains 2 or more identifiable ester functional repeat units of the same or different formula.

[0017] As used herein, a "macrocyclic oligoester" means a macrocyclic oligomer containing 2 or more identifiable ester functional repeat units of the same or different formula. A macrocyclic oligoester typically refers to multiple molecules of one specific formula having varying ring sizes. However, a macrocyclic oligoester may also include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. A macrocyclic oligoester may be a co-oligoester or multi-oligoester, i.e., an oligoester having two or more different structural repeat units having an ester functionality within one cyclic molecule.

[0018] As used herein, a "cyclic ester" means a cyclic molecule having at least one ring within its molecular structure that contains an ester functionality within the ring. A cyclic ester typically refers to multiple molecules of one specific cyclic ester. A cyclic ester as used herein is not a macrocyclic oligoester as defined above.

[0019] As used herein, "an alkylene group" means  $-C_nH_{2n}-$ , where  $n \geq 2$ .

[0020] As used herein, "a cycloalkylene group" means a cyclic alkylene group,  $-C_nH_{2n-x}-$ , where  $x$  represents the number of H's replaced by cyclization(s).

[0021] As used herein, "a mono- or polyoxyalkylene group" means  $[-(CH_2)_m-O-]_n-(CH_2)_m-$ , wherein  $m$  is an integer greater than 1 and  $n$  is an integer greater than 0.

[0022] As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

[0023] As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure therein.

[0024] As used herein, a "block copolymer" means a copolymer having segments of two or more polymers linked to one another. A block copolymer has constitutionally different structural units. Adjacent segments (i.e., blocks) contain structural units derived from different characteristic species of monomer or from structural repeat units with different composition or sequence distribution.

[0025] As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as a fibrous or particulate material. Illustrative examples of particulate material are chopped fibers, glass microspheres, and crushed stone. Certain fillers and additives thus can be used to prepare polyester polymer composites. A fibrous material

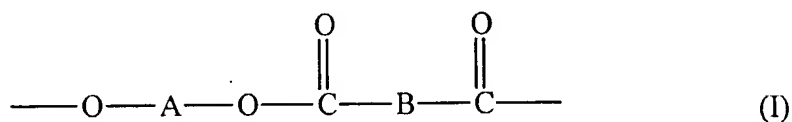
means more continuous substrate, e.g., fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

[0026] As used herein, "a divalent organic moiety" means any organic group so long as it does not interfere with the polymerization reaction of a macrocyclic oligoester and a cyclic ester. The organic moiety can be saturated or unsaturated. The organic moiety can be a hydrocarbon group or in addition can contain one or more heteroatoms. The organic moiety can be linear or branched, or contain one or more cyclic or heterocyclic structures containing one or more O, N, or S atoms. Exemplary R<sub>1</sub> and R<sub>2</sub> groups include divalent mono- or polyalkylene groups containing 1-20 carbon atoms, cycloalkylene groups containing 1-20 carbon atoms, and substituted or unsubstituted divalent aromatic groups such as phenyl groups or alicyclic groups containing 1-20 carbon atoms.

#### Copolyesters from Macrocyclic Oligoesters and Cyclic Esters

[0027] High molecular weight copolyesters have been prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst.

[0028] In one aspect, the invention generally features a method for making a copolyester. The method includes the steps of providing a macrocyclic oligoester, providing a cyclic ester other than a macrocyclic oligoester, and contacting the macrocyclic oligoester and the cyclic ester in the presence of a transesterification catalyst at an elevated temperature to produce a copolyester. The macrocyclic oligoester has a structural repeat unit of formula (I):



wherein A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group.

[0029] Polymerization reaction occurs between a macrocyclic polyester oligomer and a cyclic ester. The polymerization typically is completed within minutes. The duration of the polymerization reaction depends on many factors such as the molar ratio of macrocyclic oligoester to cyclic ester, the molar ratio of monomers (the macrocyclic oligoesters and the cyclic esters) to catalyst, the temperature at which the polymerization reaction is carried out, the desired

molecular weight, and the choice of solvent. The polymerization is preferably conducted under an inert environment, such as under nitrogen or argon, or under a vacuum.

[0030] The molar ratio of cyclic ester to macrocyclic oligoester can vary from about 0.01 to 10. In one embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 0.1 to about 1. In another embodiment, the molar ratio of cyclic ester to macrocyclic oligoester is between about 0.1 to about 0.5. The molar ratio of ester monomers (macrocyclic oligoester and cyclic ester combined) to the catalyst can range from about 500 to about 500,000. In one embodiment, the molar ratio of ester monomers to catalyst is from about 1,000 to about 500,000. In another embodiment, the molar ratio is about 1,000 to about 100,000. In yet another embodiment, the molar ratio is from about 1,000 to about 10,000.

[0031] Yields of copolyesters depend on, among other factors, the precursor monomers used, the reaction conditions, and the work-up procedure. Typical yields range from about 90% to about 98%. The resulting copolyesters typically have molecular weights from about 90k to about 150k. The temperature range of melting endotherm can be as low as about 145°C to about 180°C for high cyclic ester content to as high as about 200°C to about 230°C for low cyclic ester content. The peak temperature ranges from about 165°C to about 220°C. The heat of melting is determined by differential scanning calorimetry (DSC) to be from about 10 to about 50 Joule/g.

[0032] Copolyesters prepared according to methods of the invention show improved crystallinity and ductility as demonstrated by the temperature range of melting endotherm and the heat of melting of the resulting copolyesters. Copolyesters having a 40% caprolactone content, for example, exhibit a drastically lowered melting point range and reduced heat of melting, indicative of low crystallinity and high ductility. (See Examples which follow.)

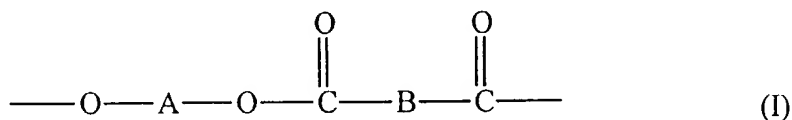
[0033] The polymerization reaction may be carried out with or without a solvent. A solvent may be used to dissolve one or more of the reactants and/or to mix the reactants. A solvent may also be used as a medium in which the reaction is carried out. Illustrative solvents that may be used include high-boiling compounds such as *o*-dichlorobenzene and meta-terphenyl. In another embodiment, no solvent is used in the polymerization reaction.

[0034] One of the precursors employed in an embodiment of the invention to prepare copolyesters is a macrocyclic oligoester. Many different macrocyclic oligoesters readily can be made and are useful in the practice of this invention. Thus, depending on the desired properties



of the final copolyester polymer product, the appropriate macrocyclic oligoester(s) can be selected for use in its manufacture.

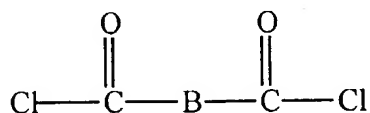
[0035] Macrocyclic oligoesters that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



wherein A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group.

[0036] Preferred macrocyclic oligoesters are macrocyclic oligoesters of 1,4-butylene terephthalate (CBT), 1,3-propylene terephthalate (CPT), 1,4-cyclohexylenedimethylene terephthalate (CCT), ethylene terephthalate (CET), and 1,2-ethylene 2,6-naphthalenedicarboxylate (CEN), and macrocyclic co-oligoesters comprising two or more of the above structural repeat units.

[0037] Synthesis of the macrocyclic oligoesters may be achieved by contacting at least one diol of the formula HO-A-OH with at least one diacid chloride of the formula:



where A and B are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such amines is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is within the range of from about -25°C to about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

[0038] Macrocyclic oligoesters also can be prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as

triethylamine. The condensation reaction is conducted in a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof. See, e.g., U.S. Patent No. 5,231,161 to Brunelle et al.

[0039] Another method for preparing macrocyclic oligoesters or macrocyclic co-oligoesters is the depolymerization of linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to macrocyclic oligoesters by heating a mixture of linear polyesters, an organic solvent, and a transesterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

[0040] It is also within the scope of the invention to employ macrocyclic co-oligoesters to produce copolyesters. Therefore, unless otherwise stated, an embodiment of a composition, article, or process that refers to macrocyclic oligoesters also includes embodiments utilizing macrocyclic co-oligoesters.

[0041] Cyclic esters employed in various embodiments of the invention include any cyclic esters that react with a macrocyclic oligoester to form a copolyester under transesterification conditions.

[0042] Cyclic esters include lactones. The lactones may be a cyclic ester of any membered ring. In one embodiment, lactones of 5-10 membered rings are used. The lactone can be unsubstituted or substituted. One or more carbon atoms in the lactone structure can be substituted with a heteroatom such as O, N, or S. One or more hydrogen atoms in the basic lactone structure can be substituted with a halogen atom (e.g., F, Cl, Br, or I) or other functional groups including alkyl groups (e.g., methyl, ethyl, propyl, butyl, etc.), a hydroxy group, alkyloxy groups, a cyano group, amino groups, and aromatic groups. The lactone can contain one or more additional rings. Illustrative examples of lactones include lactide, glycolide, dioxanone, 1,4-dioxane-2,3-dione,  $\epsilon$ -caprolactone,  $\beta$ -propiolactone, tetramethyl glycolide,  $\beta$ -butyrolactone,  $\gamma$ -butyrolactone, and pivalolactone.

[0043] Catalysts employed in the invention are those that are capable of catalyzing a transesterification polymerization of a macrocyclic oligoester with a cyclic ester. As with state-of-the-art processes for polymerizing macrocyclic oligoesters, organotin and organotitanate

compounds are the preferred catalysts, although other catalysts may be used. For example, organotin compound dibutyltin dioxide can be used as polymerization catalyst. Other illustrative organotin compounds include 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane, n-butyltin(IV) chloride dihydroxide, dialkyltin(IV) oxides, such as di-n-butyltin(IV) oxide and di-n-octyltin oxide, and acyclic and cyclic monoalkyltin (IV) derivatives such as n-butyltin tri-n-butoxide, dialkyltin(IV) dialkoxides such as di-n-butyltin(IV) di-n-butoxide and 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and trialkyltin alkoxides such as tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.* In addition, tin catalysts described in commonly owned U.S.S.N. 09/754,943 (incorporated herein by reference in its entirety) may be used in the polymerization reaction.

[0044] As for titanate compounds, tetra-isopropyl titanate may be employed in the invention. Other examples of titanate catalysts that can be used include tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds described in commonly owned U.S.S.N. 09/754,943 (incorporated herein by reference in its entirety).

[0045] The polymerization reaction is carried out at an elevated temperature. In one embodiment, the temperature is maintained within a range from about 100°C to about 300°C. In one embodiment, the temperature is maintained within a range from about 100°C to about 260°C. In another embodiment, the temperature is maintained within a range from about 150°C to about 210°C. In another embodiment, the temperature is maintained within a range from about 170°C to about 200°C. In yet another embodiment, the temperature is maintained within a range from about 180°C to about 190°C.

[0046] In another embodiment, the invention generally features a method of making a block copolymer of polyesters. Specifically, contacting a macrocyclic oligoester and a transesterification catalyst at an elevated temperature forms a first polymeric segment. Subsequently contacting the first polymeric segment, a cyclic ester that is not a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps are then sequentially repeated a desired number of times to form a block copolyester having additional first and second polymeric segments.

[0047] The above method of making a block copolymer may be modified in its sequence to begin with a cyclic ester. The polymerization may begin with a formation of a block of cyclic

ester. Thus, a first polymeric segment is formed by contacting a cyclic ester that is not a macrocyclic oligoester and a transesterification catalyst at an elevated temperature. Subsequently contacting the first polymeric segment, a macrocyclic oligoester, and the transesterification catalyst at an elevated temperature forms a second polymeric segment. The above steps are then sequentially repeated a desired number of times to form a block copolymer having additional first and second polymeric segments.

**[0048]** In one embodiment, to prepare a block copolyester having blocks derived from a macrocyclic oligoester and a cyclic ester, the macrocyclic oligoester and the cyclic ester are reacted sequentially instead of simultaneously. Depending on the applications, it may be desirable to have a block copolymer having blocks derived from both macrocyclic oligoester and cyclic ester. Thus, the method of making a block copolymer can include a step of contacting a cyclic ester and a macrocyclic oligoester in the presence of a polymerization catalyst to form a third type of block. A protocol can be designed to achieve the desired copolyester having two or more different blocks. In addition, the same or different polymerization catalysts may be used in forming the two or more different blocks in preparing a block copolyester. More than one catalyst may be employed in each of the polymerization steps.

**[0049]** In yet another aspect, the invention features a composition of a copolyester. The copolyester has, within its polymeric backbone, at least one structural unit of formula (I) and at least one structural unit of formula (II)



wherein  $R_1$  and  $R_2$  are independently a divalent organic moiety with the proviso that  $R_1$  is not  $-O-A'-$  if  $R_2$  is  $-B'-C(O)-$ .  $A'$  is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group.  $B'$  is a divalent aromatic or alicyclic group.

**[0050]** In another embodiment, the invention features a block copolymer of polyesters. The block copolymer contains at least a first block unit and a second block unit. The first block unit has, within its polymeric backbone, at least one first structural unit of formula (I). The second block unit has, within its polymeric backbone, at least one second structural unit of formula (II).

**[0051]** In one embodiment, the block copolymer contains additional blocks containing at least one structural unit of formula (I) and containing at least one structural unit of formula (II). Thus, a block copolymer may contain blocks derived from macrocyclic oligoesters, blocks derived

from cyclic esters, and blocks derived from both macrocyclic oligoesters and cyclic esters. The length of the individual blocks and the sequence thereof can be designed to serve particular applications.

[0052] The compositions and methods of the invention may be used to manufacture articles of various size and shape from various macrocyclic oligoesters and cyclic esters. Exemplary articles that may be manufactured by the invention include without limitation automotive body panels and chassis components, bumper beams, aircraft wing skins, windmill blades, fluid storage tanks, tractor fenders, tennis rackets, golf shafts, windsurfing masts, toys, rods, tubes, bars stock, bicycle forks, and machine housings.

[0053] In the manufacture of an article, various types of fillers may be included. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silicate, titanium dioxide, calcium carbonate, chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers. A filler may be added before, during, or after the polymerization reaction between a macrocyclic oligoester and a cyclic ester. Fillers can be used to prepare polyester polymer composites.

[0054] Furthermore, in the manufacture of an article additional components (e.g., additives) may be added. Illustrative additives include colorants, pigments, magnetic materials, anti-oxidants, UV stabilizers, plasticizers, fire-retardants, lubricants, and mold releases.

### **Examples**

[0055] The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention. The products obtained from these examples may be confirmed by conventional techniques such as proton and carbon-13 nuclear magnetic resonance spectroscopy, mass

spectroscopy, infrared spectroscopy, differential scanning calorimetry and gel permeation chromatography analyses.

#### *Example A*

[0056] The macrocyclic oligoesters used in the following examples are the macrocyclic oligoesters of 1,4-butylene terephthalate. The macrocyclic oligoesters were prepared by heating a mixture of polyester linears, organic solvents, such as *o*-xylene and *o*-dichlorobenzene, which are substantially free of oxygen and water, and tin or titanium compounds as transesterification catalysts. See U.S. Patent No. 5,668,186 (incorporated herein by reference in its entirety).

#### *Example 1*

[0057] A small vial (21 x 70 mm, 4 dram), equipped with a 2.5 cm magnetic stirring bar and an argon/vacuum adapter, was charged with 2.0 g of macrocyclic oligoesters of 1,4-butylene terephthalate. The vial was then connected to vacuum and immersed into an oil bath at 190°C. Upon melting, the molten liquid was dried for 3 minutes under 1 mm vacuum. The vacuum was then released with argon. Under argon, predetermined amount (51.9 mg to 415 mg) of  $\epsilon$ -caprolactone (dried over molecular sieves) was added via a syringe. The mixture was stirred for one minute at 190°C under argon. A predetermined amount (0.30 mole %) of tin catalyst Fomrez® SUL-11A was then added as a solution in *o*-dichlorobenzene. Fomrez® SUL-11A is a 1:1 reaction product of dibutyltin dioxide/DIOP plasticizer available from Witco Chemicals (Crompton Corporation). The resulting reaction mixture became viscous. Stirring stopped within about 5 to 10 seconds. After 15 minutes, the vial was removed from the oil bath and was immediately cooled with ice-water. The vial was broken to retrieve a sample of the polymer. After dissolution in 15% hexfluoroisopropanol/chloroform, the sample was analyzed by gel permeation chromatography (GPC). The test results are shown in Table 1.

**Table 1. Co-Polymerization Of Macrocyclic Oligoesters CBT  
With  $\epsilon$ -Caprolactone Using A Tin Catalyst**

$\epsilon$ -Caprolactone/CBT (Molar Ratio)	% Polymer	Mw <sup>a</sup>	T <sub>m</sub> (°C) <sup>b</sup>	Temp. Range Of Melting Endotherm (°C)	$\Delta H^c$ (J/g)
00/100	94	132,300	221	198-230	49.7
05/100	96	140,180	214	200 - 220	43.9
15/100	96	139,680	196	175 - 220	23.1
20/100	98	121,850	190	175 - 220	24.7
25/100	97	134,490	185	160 - 220	19.8
30/100	97	130,400	177	160 - 190	17.8
35/100	98	128,800	170	150 - 180	14.4
40/100	92	136,000	164	145 - 180	11.8

<sup>a</sup> Molecular weight (by GPC relative to polystyrene standards)

<sup>b</sup> Peak temperature of the melting endotherm (by DSC with heating rate of 20°C/min)

<sup>c</sup> Heat of melting (DSC with a heating rate of 20°C/min)

### **Example 2**

[0058] A small vial (21 x 70 mm, 4 dram), equipped with a 2.5 cm magnetic stirring bar and argon/vacuum adapter, was charged with 2.0 g of macrocyclic oligoesters of 1,4-butylene terephthalate. The vial was then connected to vacuum and immersed into an oil bath at 190°C. Upon melting, the molten liquid was dried for 3 minutes under 1 mm vacuum. The vacuum was then released with argon. Under argon, predetermined amount (51.9 mg to 415 mg) of  $\epsilon$ -caprolactone (dried over molecular sieves) was added via a syringe. The mixture was stirred for one minute at 190°C under argon. A predetermined amount (0.30 mole %) of titanate catalyst Tyzor® TPT was then added as a solution in *o*-dichlorobenzene. Tyzor® TPT is tetra-isopropyl titanate available from E.I. du Pont Nemours and Company (Wilmington, Delaware). The resulting reaction mixture became viscous. Stirring stopped within about 5 to 10 seconds. After 15 minutes, the vial was removed from oil bath, and was immediately cooled with ice-water. The vial was then broken to retrieve a sample of the polymer. After dissolution in 15% hexfluoroisopropanol/chloroform, the sample was analyzed by GPC. The test results are shown in Table 2.

**Table 2. Co-Polymerization Of Macrocyclic Oligoesters CBT  
With  $\epsilon$ -Caprolactone Using A Titanate Catalyst**

$\epsilon$ -Caprolactone/CBT (Molar Ratio)	% Polymer	Mw <sup>a</sup>	T <sub>m</sub> (°C) <sup>b</sup>	Temp. Range Of Melting Endotherm (°C)	$\Delta H^c$ (J/g)
25/100	98%	95,000	190	170-200	13.0

<sup>a</sup> Molecular weight (by GPC relative to polystyrene standards)

<sup>b</sup> Peak temperature of the melting endotherm (by DSC with heating rate of 20°C/min)

<sup>c</sup> Heat of melting (by DSC with heating rate of 20°C/min)

[0059] Each of the patent documents disclosed hereinabove is incorporated by reference herein in their entirety. Variations, modifications, and other implementations of what is described herein will occur to those of ordinary skill in the art without departing from the spirit and the scope of the invention as claimed. Accordingly, the invention is to be defined not by the preceding illustrative description but instead by the spirit and scope of the following claims.

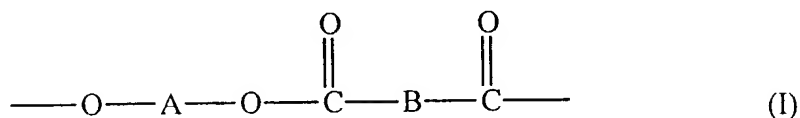


## CLAIMS

What is claimed is:

1. A method of making a copolyester, the method comprising the steps of:

- (a) providing a macrocyclic oligoester having a structural repeat unit of formula (I):



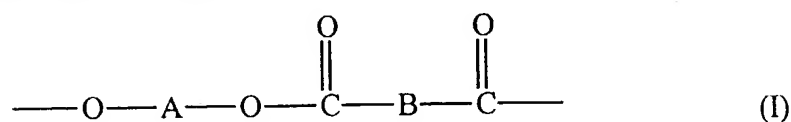
wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;  
and

B is a divalent aromatic or alicyclic group;

- (b) providing a cyclic ester, wherein the cyclic ester is not a macrocyclic oligoester;  
and
  - (c) contacting the macrocyclic oligoester and the cyclic ester in the presence of a transesterification catalyst at an elevated temperature to produce the copolyester.
2. The method of claim 1 wherein the cyclic ester is a lactone.
  3. The method of claim 2 wherein the lactone is  $\epsilon$ -caprolactone.
  4. The method of claim 1 wherein the macrocyclic oligoester comprises macrocyclic oligo(1,4-butylene terephthalate).
  5. The method of claim 1 wherein the macrocyclic oligoester comprises macrocyclic oligo(ethylene terephthalate).
  6. The method of claim 1 wherein the transesterification catalyst comprises a tin compound.
  7. The method of claim 6 wherein the tin compound is a dialkyltin oxide.
  8. The method of claim 1 wherein the transesterification catalyst comprises a titanate compound.
  9. The method of claim 8 wherein the titanate compound is an alkyl titanate.
  10. The method of claim 1 wherein the elevated temperature is within a temperature range from about 100 °C to about 300 °C.

11. The method of claim 1 wherein the elevated temperature is within a temperature range from about 100°C to about 260°C.
12. The method of claim 1 wherein the elevated temperature is within a temperature range from about 150 °C to about 210°C.
13. A method of making a block copolymer of polyesters, the method comprising the steps of:
  - (a) contacting a macrocyclic oligoester and a transesterification catalyst at an elevated temperature to form a first polymeric segment, wherein the macrocyclic oligoester has a structural repeat unit of formula (I):



wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

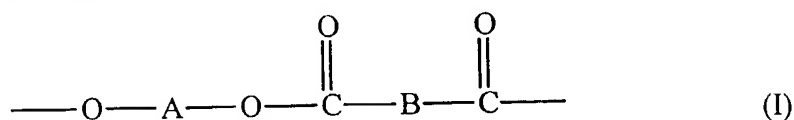
and

B is a divalent aromatic or alicyclic group;

- (b) contacting a cyclic ester, the first polymeric segment, and the transesterification catalyst at an elevated temperature to form a second polymeric segment, wherein the cyclic ester is not a macrocyclic oligoester; and
  - (c) sequentially repeating steps (a) and (b) a desired number of times to form a block copolymer having additional first and second polymeric segments.
14. The method of claim 13 wherein the cyclic ester is a lactone.
15. The method of claim 13 wherein the macrocyclic oligoester is macrocyclic oligo(1,4-butylene terephthalate).
16. The method of claim 13 wherein the transesterification catalyst comprises a tin compound.
17. The method of claim 13 wherein the transesterification catalyst comprises a titanate compound.
18. The method of claim 13 wherein the elevated temperature is within a temperature range from about 100°C to about 300°C.

19. A method of making a block copolymer of polyesters, the method comprising the steps of:

- (a) contacting a cyclic ester and a transesterification catalyst at an elevated temperature to form a first polymeric segment, wherein the cyclic ester is not a macrocyclic oligoester; and
- (b) contacting a macrocyclic oligoester, the first polymeric segment, and the transesterification catalyst at an elevated temperature to form a second polymeric segment, wherein the macrocyclic oligoester has a structural unit of formula (I)



wherein

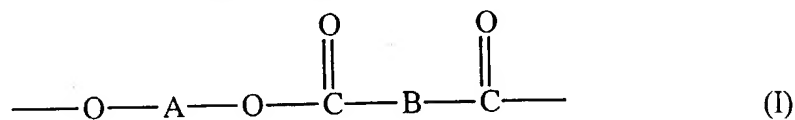
A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group,  
and

B is a divalent aromatic or alicyclic group; and

- (c) sequentially repeating steps (a) and (b) a desired number of times to form a block copolymer having additional first and second polymeric segments.

20. A copolyester comprising, within its polymeric backbone,

- (a) at least one structural unit of formula (I)



wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group,  
and

B is a divalent aromatic or alicyclic group; and

- (b) at least one structural unit of formula (II)



wherein

R<sub>1</sub> and R<sub>2</sub> are independently a divalent organic moiety with the proviso that R<sub>1</sub> is not  $\text{---O---A'---}$  if R<sub>2</sub> is  $\text{---B'---C(O)---}$

wherein

A' is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

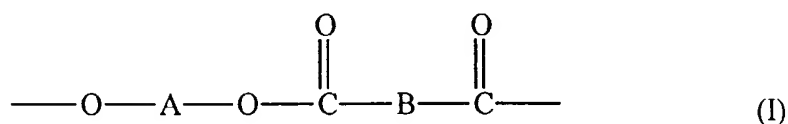
B' is a divalent aromatic or alicyclic group.

21. The copolyester of claim 20 wherein A is 1,4-butylene and B is benzene.

22. The copolyester of claim 20 wherein A is ethylene and B is benzene.

23. A block copolymer comprising

- (a) a first block unit comprising, within its polymeric backbone, at least one structural unit of formula (I)



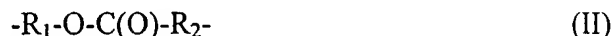
wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group,

and

B is a divalent aromatic or alicyclic group; and

- (b) a second block unit comprising, within its polymeric backbone, at least one structural unit of formula (II)



wherein

R<sub>1</sub> and R<sub>2</sub> are independently a divalent organic moiety with the proviso that R<sub>1</sub> is not -O-A'- if R<sub>2</sub> is -B'-C(O)-

wherein

A' is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group;

and

B' is a divalent aromatic or alicyclic group.

24. A copolyester prepared by the method of claim 1.

25. A block copolymer of polyesters prepared by the method of claim 14.

26. A block copolymer of polyesters prepared by the method of claim 19.

27. An article of manufacture comprising the copolyester of claim 20.

28. A composite material comprising the block copolymer of claim 23.

29. An article of manufacture comprising the block copolymer of claim 23.

## HIGH MOLECULAR WEIGHT COPOLYESTERS FROM MACROCYCLIC OLIGOESTERS AND CYCLIC ESTERS

### Abstract of the Disclosure

High molecular weight copolyesters have been prepared from macrocyclic oligoesters and cyclic esters in the presence of a transesterification catalyst. The invention generally features a method of making a copolyester, a method of making a block copolymer of copolyester, and a copolyester prepared from macrocyclic oligoesters and cyclic esters.

2059425-1



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APPLICATION NUMBER	FILING DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO	DRAWINGS	TOT CLAIMS	IND CLAIMS
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## Continuing Data as Claimed by Applicant

THIS APPLICATION IS A CIP OF 09/535,132 03/24/2000  
AND CLAIMS BENEFIT OF 60/177,727 01/21/2000

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## Title

Macrocyclic polyester oligomers and processes for polymerizing the same

## Preliminary Class

PATENT

Atty. Docket No.: CYC-035 (1591/15)

A BLEND MATERIAL INCLUDING MACROCYCLIC POLYESTER OLIGOMERS AND  
PROCESSES FOR POLYMERIZING THE SAME

Related Applications

[0001] This application is a continuation-in-part of U.S. Utility Patent Application Serial No. 09/535,132 (Attorney Docket No. CYC-034) filed on March 24, 2000. This application also claims the benefit of the filing date of U.S. Provisional Patent Application Serial No. 60/177,727, filed on January 21, 2000, entitled "Processing with Cyclic PBT to Produce Thermoplastic Compositions" by Winckler. The entirety of these applications is incorporated herein by reference.

Technical Field

[0002] This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to a blend material prepared from a macrocyclic polyester oligomer and a polymerization catalyst, and processes of using the same.

Background Information

[0003] Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. They have many valuable characteristics including strength, toughness, high gloss and solvent resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding.



[0004] Recently, macrocyclic polyester oligomers were developed which have unique properties. These properties make them attractive as matrices for engineering thermoplastic composites. These desirable properties stem from the fact that macrocyclic polyester oligomers exhibit low melt viscosity, allowing them to impregnate a dense fibrous preform easily. Furthermore, certain macrocyclic polyester oligomers melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate catalyst, polymerization and crystallization can occur virtually isothermally. As a result, the time and expense required to thermally cycle a tool is favorably reduced.

[0005] Development of processing equipment for use with macrocyclic polyester oligomers has been limited. It is generally believed that production of molded parts from macrocyclic polyester oligomers requires existing equipment to be modified to allow for transfer of the macrocyclic polyester oligomers and polymerization catalysts into the equipment in the appropriate amounts at the appropriate time and at the appropriate temperature. Modifying existing equipment takes time and is often costly, and hence limits the application of macrocyclic polyester oligomers.

#### Summary of the Invention

[0006] A blend of a macrocyclic polyester oligomer and a polymerization catalyst as a one component ready-to-use material with a long shelf life enables production of parts from macrocyclic polyester oligomers without the modification of existing equipment, thereby reducing time and cost of manufacture while expanding the application of macrocyclic polyester oligomers. In this blend material, the macrocyclic polyester oligomer remains intact in solid state at ambient conditions. Upon melting, the blend material initially forms a low viscosity fluid, and then rapidly polymerizes to form high molecular weight polyesters which subsequently solidify to form semi-crystalline polymers. In the case of certain macrocyclic polyester oligomers, for example, poly(1,4-butylene terephthalate), demolding can take place at the polymerization temperature, e.g., at about 180°C to 200°C, because the resulting polyester polymer solidifies fairly rapidly at that temperature without cooling.

[0007] In one aspect, the invention generally features a blend material that includes a macrocyclic polyester oligomer, a polymerization catalyst, and optionally, a filler. In one embodiment, the macrocyclic polyester oligomer is substantially a homo- or co-polyester

oligomer. Polymerization catalysts include, among others, tin compounds and titanate compounds.

[0008] In another aspect, the invention generally features a process for preparing a blend material as described above.

[0009] In yet another aspect, the invention features processes such as rotational molding, resin film infusion, pultrusion, resin transfer molding, filament winding, making and using powder coated or hot melt prepreg, compression molding, roll wrapping, and water slurry, which use the blend material described above. These processes of the invention may be used to form polyester polymer composites which may be included in articles of manufacture such as carbon fiber golf shafts or lightweight automotive chassis members.

[0010] In one aspect, a water slurry process is used to prepare a prepreg and to manufacture articles from macrocyclic polyester oligomers. In one embodiment, a process for preparing a water suspension of macrocyclic polyester oligomers includes the steps of contacting a macrocyclic polyester oligomer and a polymerization catalyst with water and a surfactant, and mixing the macrocyclic polyester oligomer and polymerization catalyst with water and the surfactant thereby forming a suspension. In another embodiment, a process for impregnating macrocyclic polyester oligomers for polymerization includes the steps of providing a suspension of a macrocyclic polyester oligomer and a polymerization catalyst in water, applying the suspension to a base material, drying to remove water from the suspension, and pressing the dried suspension to a desired form. In yet another embodiment, a composition of macrocyclic polyester oligomer includes a macrocyclic polyester oligomer, a polymerization catalyst, and water. In yet another embodiment, a process for polymerizing macrocyclic polyester oligomers includes the steps of mixing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst with water to form a mixture, applying the mixture to a base material, drying to remove water, heating to polymerize the macrocyclic polyester oligomer, and pressing the polymerized macrocyclic polyester oligomer to a desired form.

[0011] Thus, heating may be applied such that, after drying the mixture, there is no polymerization, partial polymerization or complete polymerization of the macrocyclic polyester oligomer.

[0012] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following figures, description, and claims.

#### Brief Description of Figures

[0013] The drawings are not necessarily to scale, emphasis instead is generally placed upon illustrating the principles of the invention to facilitate its understanding.

FIG. 1 is a schematic illustration of an embodiment of the invention including a rotational molding process.

FIG. 2 is a schematic illustration of an embodiment of the invention including a resin film infusion process.

FIG. 3 is a schematic illustration of an embodiment of the invention including a solvent prepreg process.

FIG. 4 is a schematic illustration of an embodiment of the invention including a hot-melt prepreg process.

FIG. 5 is a schematic illustration of an embodiment of the invention including a pultrusion process.

FIG. 6 is a schematic illustration of an embodiment of the invention including an extruder.

FIG. 7 is a schematic illustration of an embodiment of the invention including a piston type continuous melter.

FIG. 8 is a schematic illustration of an embodiment of the invention including a resin transfer molding process.

FIG. 9 is a schematic illustration of an embodiment of the invention including a filament winding process.

FIG. 10 is a schematic illustration of an embodiment of the invention including a compression molding process.

FIG. 11 is a schematic illustration of an embodiment of the invention including a roll wrapping process.

FIG. 12 is a schematic illustration of an embodiment of the invention including a powder coating process.

FIG. 13 is a schematic illustration of an embodiment of the invention including a water slurry process.

FIG. 14 is a schematic illustration of another embodiment of the invention including a water slurry process.

#### Description

[0014] The present invention is directed to the surprising discovery that a blend material comprising a macrocyclic polyester oligomer and a polymerization catalyst provides superior processing characteristics relative to conventional thermoplastics precursors. Prior to this invention, it was not recognized that a mixture of a macrocyclic polyester oligomer and a polymerization catalyst can be stable and have a long shelf life. The blend material of the invention allows for easy production, storage, transportation and processing.

[0015] From the standpoint of applications, the blend material is one-component and is ready to-use. The blend material may be used advantageously for manufacturing articles using processes such as injection and rotational molding, resin film infusion, resin transfer molding, filament winding, powder coating to create a prepreg or film, hot melt prepreg preparation, compression molding, roll wrapping, water slurry, and pultrusion with or in some cases without reinforcement. The blend material may also be processed like a thermoset while producing a thermoplastic product. Furthermore, the blend material eliminates the need to modify existing equipment to allow for transfer of the macrocyclic polyester oligomer and the polymerization catalyst into the equipment in the appropriate amounts at the appropriate time and at the appropriate temperature. Accordingly, this invention provides for ways to achieve greater production efficiency and lower manufacturing costs.

#### Definitions

[0016] The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

[0017] As used herein, a "blend material" is understood to mean a mixture of two or more components including at least one macrocyclic polyester oligomer and at least one

FIG. 13 is a schematic illustration of an embodiment of the invention including a water slurry process.

FIG. 14 is a schematic illustration of another embodiment of the invention including a water slurry process.

### Description

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[0017] As used herein, a "blend material" is understood to mean a mixture of two or more components including at least one macrocyclic polyester oligomer and at least one

polymerization catalyst. Preferably the blend material is uniformly mixed. A blend material may also include a filler as well as other components recognized by a skilled artisan.

[0018] As used herein, "macrocyclic" is understood to mean a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

[0019] As used herein, an "oligomer" is understood to mean a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

[0020] As used herein, a "macrocyclic polyester oligomer" is understood to mean a macrocyclic oligomer containing structural repeat units having an ester functionality. A macrocyclic polyester oligomer typically refers to multiple molecules of one specific formula. However, a macrocyclic polyester oligomer also may include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. In addition, a macrocyclic polyester oligomer may be a co-polyester or multi-polyester oligomer, i.e., an oligomer having two or more different structural repeat units having an ester functionality within one cyclic molecule.

[0021] As used herein, "substantially homo- or co-polyester oligomer" is understood to mean a polyester oligomer wherein the structural repeat units are substantially identical or substantially two different structural repeat units, respectively.

[0022] As used herein, "an alkylene group" is understood to mean  $-C_nH_{2n}-$ , where  $n \geq 2$ .

[0023] As used herein, "a cycloalkylene group" is understood to mean a cyclic alkylene group,  $-C_nH_{2n-x}-$ , where x represents the number of H's replaced by cyclization(s).

[0024] As used herein, "a mono- or polyoxyalkylene group" is understood to mean  $[-(CH_2)_m-O-]_n-(CH_2)_m-$ , wherein m is an integer greater than 1 and n is an integer greater than 0.

[0025] As used herein, "a divalent aromatic group" is understood to mean an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

[0026] As used herein, "an alicyclic group" is understood to mean a non-aromatic hydrocarbon group containing a cyclic structure within.

[0027] As used herein, "a  $C_{1-4}$  primary alkyl group" is understood to mean an alkyl group having 1 to 10 carbon atoms which includes straight chain or branched molecules.

[0028] As used herein, "a C<sub>1-10</sub> alkyl group" is understood to mean an alkyl group connected via a primary carbon atom.

[0029] As used herein, a "methylene group" is understood to mean -CH<sub>2</sub>-.

[0030] As used herein, an "ethylene group" is understood to mean -CH<sub>2</sub>-CH<sub>2</sub>-.

[0031] As used herein, "a C<sub>2-3</sub> alkylene group" is understood to mean -C<sub>n</sub>H<sub>2n</sub>-, where n is 2 or 3.

[0032] As used herein, "a C<sub>2-6</sub> alkylene group" is understood to mean -C<sub>n</sub>H<sub>2n</sub>-, where n is 2-6.

[0033] As used herein, "substitute phenyl group" is understood to mean a phenyl group having one or more substituents. A substituted phenyl group may have substitution pattern that is recognized in the art. For example, a single substituent may be in the ortho, meta or para positions. For multiple substituents, typical substitution patterns include, for example, 2,6-, 2,4,6-, and, 3,5- substitution patterns.

[0034] As used herein, "a filler" is understood to mean a material other than a macrocyclic polyester oligomer or a polymerization catalyst that may be included in the blend material. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silica, titanium dioxide, calcium carbonate, chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers.

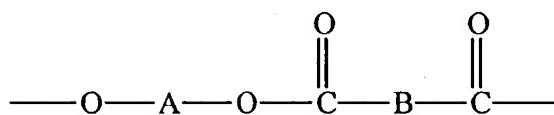
[0035] As used herein, "a polyester polymer composite" is understood to mean a polyester polymer that is associated with another substrate such as, a fibrous or particulate material. Illustrative examples of particulate material are chopped fibers, glass microspheres, and crushed stone. Certain fillers thus can be used to prepare polyester polymer composites.

[0036] As used herein, a "fibrous substrate" is understood to mean more continuous substrate, e.g., fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

# **I. Macrocyclic Polyester Oligomers**

[0037] One of the ingredients of the blend material of the invention is a macrocyclic polyester oligomer. Many different macrocyclic polyester oligomers can readily be made and are useful in the practice of this invention. Thus, depending on the desired properties of the final polyester polymer product, the appropriate macrocyclic polyester oligomer(s) can be selected for use in its manufacture.

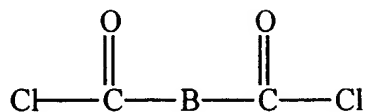
[0038] Macrocyclic polyester oligomers that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group.

[0039] Preferred macrocyclic polyester oligomers are macrocyclic poly(1,4-butylene terephthalate) (PBT), poly(1,3-propylene terephthalate) (PPT), poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), poly(ethylene terephthalate) (PET), and poly(1,2-ethylene 2,6-naphthalenedicarboxylate) (PEN) oligomers, and copolyester oligomers comprising two or more of the above monomer repeat units.

[0040] Macrocyclic polyester oligomers may be prepared by known methods. Synthesis of the preferred macrocyclic polyester oligomers may include the step of contacting at least one diol of the formula HO-A-OH with at least one diacid chloride of the formula:



where A and B are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such amines is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible



organic solvent such as methylene chloride. The temperature of the reaction typically is between about -25°C and about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

[0041] Macrocyclic polyester oligomers have also been prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as triethylamine, in a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

[0042] Another method for preparing macrocyclic polyester oligomers or macrocyclic copolyester oligomers is to depolymerize linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to macrocyclic polyester oligomers by heating a mixture of linear polyesters, an organic solvent, and a transesterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

[0043] It is also within the scope of the invention to employ macrocyclic homo- and copolyester oligomers to produce homo- and co-polyester polymers, respectively. Therefore, unless otherwise stated, an embodiment of a composition, article, or process that refers to a macrocyclic polyester oligomer also includes co-polyester embodiments.

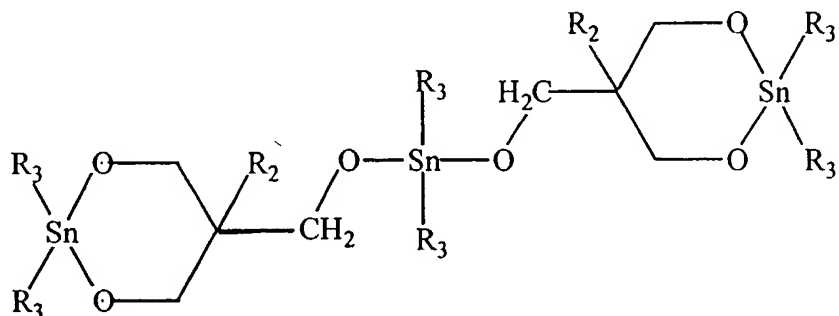
## **II. Polymerization catalysts**

[0044] The other primary ingredient of the blend material of the invention is a polymerization catalyst. The polymerization catalysts that may be employed in the invention are capable of catalyzing the polymerization of the macrocyclic polyester oligomer. As with state-of-the-art processes for polymerizing macrocyclic polyester oligomers, organotin and organotitanate compounds are the preferred catalysts, although other catalysts may be used. For example, organotin compound 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane may be used as polymerization catalyst. Other illustrative organotin compounds include *n*-butyltin(IV) chloride dihydroxide, dialkyltin(IV) oxides, such as di-*n*-butyltin(IV) oxide and di-*n*-octyltin oxide, and acyclic and cyclic monoalkyltin (IV) derivatives such as *n*-butyltin tri-*n*-butoxide, dialkyltin(IV) dialkoxides such as di-*n*-butyltin(IV) di-*n*-butoxide and 2,2-di-*n*-butyl-2-stanna-

1,3-dioxacycloheptane, and trialkyltin alkoxides such as tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.*

[0045] Also, trisstannoxanes having the general formula (I) shown below can be used as a polymerization catalyst to produce branched polyester polymers.

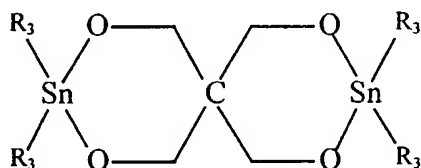
(I)



where  $R_2$  is a  $C_{1-4}$  primary alkyl group and  $R_3$  is  $C_{1-10}$  alkyl group.

[0046] Additionally, organotin compounds with the general formula (II) shown below can be used as a polymerization catalyst to prepare branched polyester polymers from macrocyclic polyester oligomers.

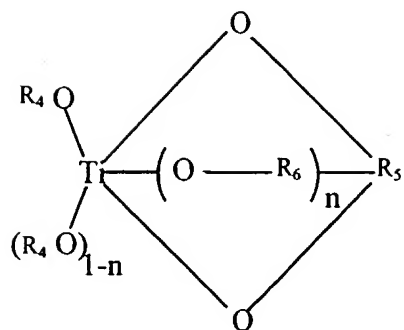
(II)



where  $R_3$  is defined as above.

[0047] As for titanate compounds, tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds with the general formula (III) shown below can be used as polymerization catalysts.

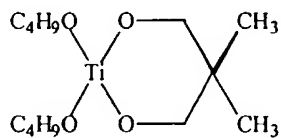
(III)



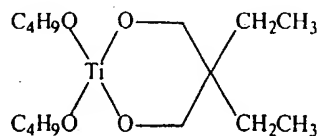
wherein: each  $\text{R}_4$  is independently an alkyl group, or the two  $\text{R}_4$  groups taken together form a divalent aliphatic hydrocarbon group;  $\text{R}_5$  is a  $\text{C}_{2-10}$  divalent or trivalent aliphatic hydrocarbon group;  $\text{R}_6$  is a methylene or ethylene group; and  $n$  is 0 or 1.

[0048] Examples of titanate compounds with the above general formula are shown in Table 1.

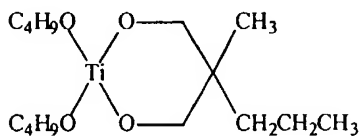
**Table 1.** Examples of Titanate Compounds Having Formula (III)



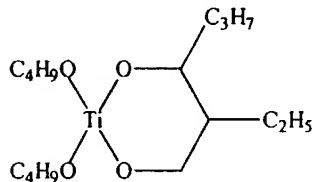
Di-1-butyl 2,2-dimethylpropane-1,3-dioxytitanate



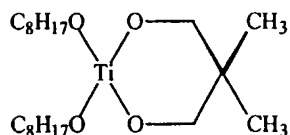
Di-1-butyl 2,2-diethylpropane-1,3-dioxytitanate



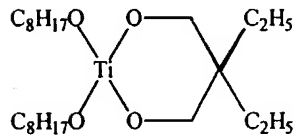
Di-1-butyl 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate



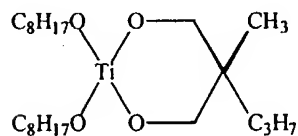
Di-1-butyl 2-ethylhexane-1,3-dioxytitanate



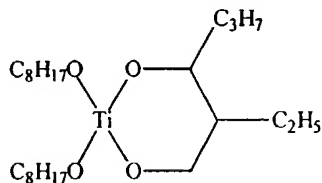
Di(2-ethyl-1-hexyl) 2,2-dimethylpropane-1,3-dioxytitanate



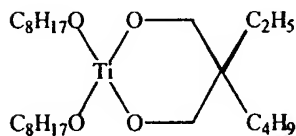
Di(2-ethyl-1-hexyl) 2,2-diethylpropane-1,3-dioxytitanate



Di(2-ethyl-1-hexyl) 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate

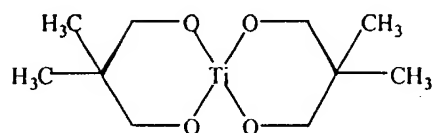


Di(2-ethyl-1-hexyl) 2-ethylhexane-1,3-dioxytitanate

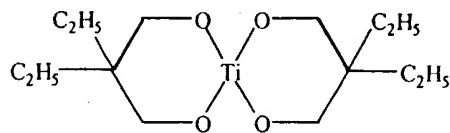


Di(2-ethyl-1-hexyl) 2-(1-butyl)-2-ethylpropane-1,3-dioxytitanate

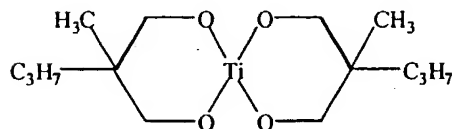
**Table 1.** Examples of Titanate Compounds Having Formula (III) (Cont'd)



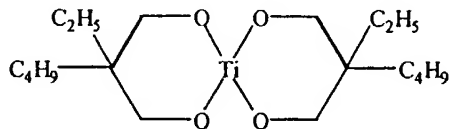
Bis(2,2-dimethyl-1,3-propylene) titanate



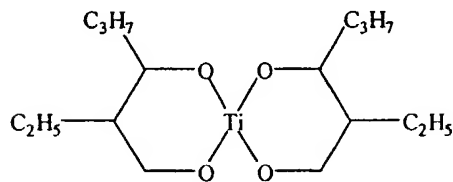
Bis(2,2-diethyl-1,3-propylene) titanate



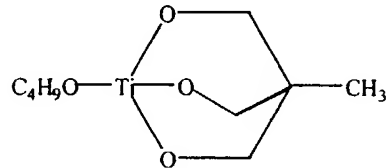
Bis(2-(1-propyl)-2-methyl-1,3-propylene) titanate



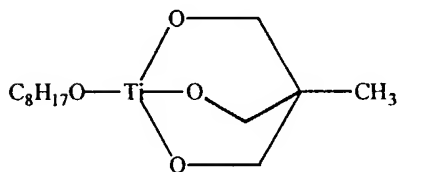
Bis(2-(1-butyl)-2-ethyl-1,3-propylene) titanate



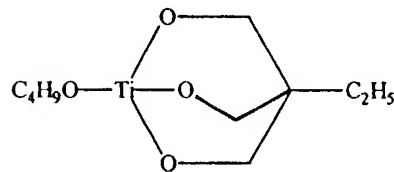
Bis(2-ethyl-1,3-hexylene) titanate



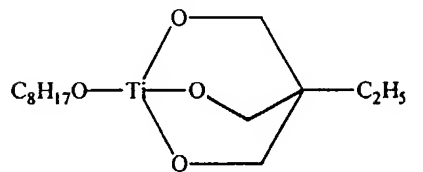
1-(1-Butoxy)-4-methyl-2,6,7-trioxal-titanabicyclo[2,2,2]octane



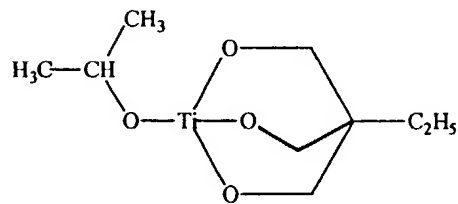
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1-(1-Butoxy)-4-ethyl-2,6,7-trioxal-titanabicyclo[2,2,2]octane



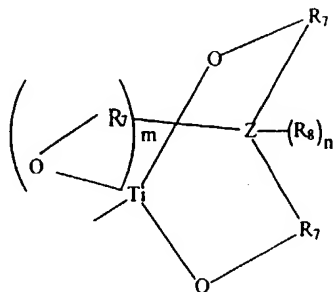
1-(2-ethyl-1-hexoxy)-4-ethyl-2,6,7-trioxal-titanabicyclo[2,2,2]octane



1-(2-Propoxy)-4-ethyl-2,6,7-trioxal-titanabicyclo[2,2,2]octane

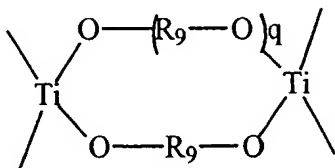
[0049] Titanate ester compounds having at least one moiety of the following general formula have also been used as polymerization catalysts:

(IV)



or

(V)



wherein:

each  $R_7$  is independently a  $C_{2-3}$  alkylene group;

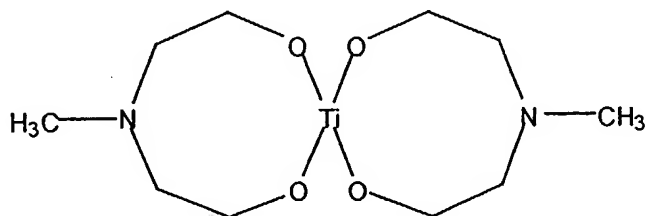
$R_8$  is a  $C_{1-6}$  alkyl group or unsubstituted or substituted phenyl group;

Z is O or N; provided when Z is O,  $m = n = 0$ , and when Z is N,  $m = 0$  or 1 and  $m + n = 1$ ;

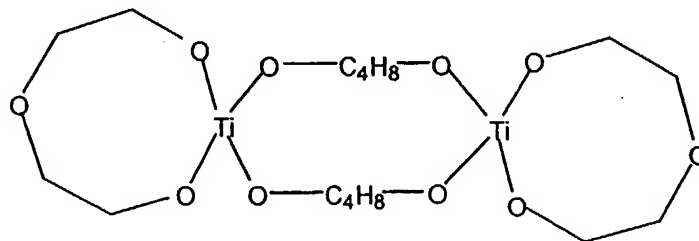
each  $R_9$  is independently a  $C_{2-6}$  alkylene group; and q is 0 or 1.

[0050] Typical examples of such titanate compounds are shown below as formula (VI) and formula (VII):

(VI)



(VII)



### **III. The Blend Material**

[0051] This invention provides a blend material and processes for preparing the blend material which includes a macrocyclic polyester oligomer and a polymerization catalyst. The blend material allows for easy production, storage, transportation and processing. From the standpoint of applications, the blend material is a one-component ready-to-use mixture. The blend material may also be processed like a thermoset while producing a thermoplastic. Furthermore, the blend material eliminates the need that existing equipment be modified to allow for transfer of the macrocyclic polyester oligomer and a polymerization catalyst into the equipment in the appropriate amounts at the appropriate time and at the appropriate temperature.

[0052] There is no limitation with respect to the physical form of the macrocyclic polyester oligomer when mixed with the polymerization catalyst as long as the macrocyclic polyester oligomer remains substantially chemically intact. In one embodiment, the macrocyclic polyester oligomer is a solid such as a powder. In this embodiment, mechanical mixing typically is used to mix the macrocyclic polyester oligomer with a polymerization catalyst. In another embodiment, the macrocyclic polyester oligomer is mixed in the presence of a solvent with the solvent remaining present during the step of mixing.

[0053] In one embodiment, the blend material also includes a filler. Illustrative examples of such fillers include pigments, light weight fillers, flame retardants, and ultraviolet light stabilizers. For example, calcium carbonate may be used to increase the thickness of a polyester polymer product to improve its mechanical performance. Also, glass microspheres may be added to lower the density of the product. Other fillers include nanoclays, e.g., to increase the modulus of the product, organo bromides in combination with antimony oxides, e.g., to impart flame resistance, and colorants such as carbon black or titanium dioxide. Fillers thus can be used to prepare polyester polymer composites.

[0054] The filler is added generally between about 0.1% and 70% by weight, between about 25% and 70% by weight, or between about 2% and 5% by weight depending on the filler and the purpose for adding the filler. For example, the percentage is preferably between 25% and 50% by weight in the case of calcium carbonate, between 2% and 5% by weight in the case of

nanoclays, between 0.1% and 1% in the case of pigments, and between 25% and 70% by weight in the case of glass microspheres.

[0055] A process for preparing the blend material includes providing a macrocyclic polyester oligomer and mixing the macrocyclic polyester oligomer with a polymerization catalyst. When preparing the blend, the macrocyclic polyester oligomer and the polymerization catalyst may be mixed together by various means. For example, any conventional mixer or blender may be employed to mix the macrocyclic polyester oligomer with the polymerization catalyst via agitation at temperatures below the melting temperature of the macrocyclic polyester oligomer. This process may be conducted under an inert atmosphere such as a nitrogen atmosphere.

[0056] A solvent may also be employed to assist in the uniform mixing of the macrocyclic polyester oligomer with the polymerization catalyst. Various solvents can be used, and there is no limitation with respect to the type of solvent that may be used other than that the solvent is substantially free of water. Illustrative examples of solvents that may be employed in the invention include methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, benzene, toluene, *o*-xylene, chlorobenzene, dichloromethane, and chloroform.

[0057] There is no limitation with respect to the amount of solvent to be employed other than that the amount results in a uniform mixing of the macrocyclic polyester oligomer and the polymerization catalyst. In one embodiment, the blend of macrocyclic polyester oligomer with the polymerization catalyst is isolated either by direct removal of the solvent via evaporation or by precipitation via addition of the mixture into a nonsolvent. In another embodiment, the blend of solid ingredients is further dried under vacuum at elevated temperatures below the melting temperature and the polymerization temperature of the macrocyclic polyester oligomer to remove any residual solvent.

[0058] A process for preparing the blend material further having at least one filler, or any other additional material, is generally the same as described above, however, the characteristics of the filler and/or additional materials must be considered. It should be understood that the macrocyclic polyester oligomer, the polymerization catalyst, the filler, any additional material(s) and/or solvent, if used, may be mixed in any order or simultaneously as long as the final composition contains the appropriate amount of each ingredient.



[0059] It is within the scope of the invention to employ one, two or more different fillers in preparing a blend material of macrocyclic polyester oligomer and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to filler in singular also includes an embodiment wherein two or more different fillers are employed. Similarly, unless stated otherwise, any embodiment of a composition, article or process that refers to fillers in plural also includes an embodiment wherein one filler is employed.

[0060] In one embodiment of the invention, the amount of polymerization catalyst employed is generally about 0.01 to about 10.0 mole percent, preferably about 0.1 to about 2 mole percent, and more preferably about 0.2 to about 0.6 mole percent based on total moles of monomer repeat units of the macrocyclic polyester oligomer.

[0061] Although dependent on the particular composition of the blend material, blend materials typically exhibit a shelf life generally longer than a week, and preferably longer than a month, and more preferably longer than a year when stored at ambient temperature.

[0062] It is within the scope of the invention to employ one, two or more different polymerization catalysts in preparing a blend of macrocyclic polyester oligomer and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to polymerization catalyst in singular also includes an embodiment wherein two or more different polymerization catalysts are employed. Similarly, unless stated otherwise, any embodiment of a composition, article or process that refers to polymerization catalyst in plural also includes an embodiment wherein one polymerization catalyst is employed. Two or more polymerization catalysts may be used to vary the rate of polymerization and to produce polyesters with variable degrees of branching.

#### **IV. Polyermizing Macrocyclic Polyester Oligomers**

[0063] In some aspects of the invention, various processes are employed to polymerize a macrocyclic polyester oligomer. For many of these processes, the unique properties of the macrocyclic polyester oligomers make it possible to use these processes advantageously. Generally, it was not previously contemplated that the use of macrocyclic polyester oligomers with these processes would in any way be advantageous.

**[0065]** In one embodiment, a process for preparing a high molecular weight polyester polymer includes providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst, and polymerizing the macrocyclic polyester oligomer. The blend material may include a filler. The filler may also be added prior to, during, or after the polymerization process. Any reaction vessel may be employed that is substantially inert to the ingredients of the blend material.

**[0067]** Examples of polyesters produced by the processes of the invention include poly(ethylene terephthalate), poly(1,3-propylene terephthalate), poly(1,4-butylene terephthalate), poly(1,4-cyclohexylenedimethylene terephthalate), poly(1,2-ethylene 2,6-naphthalenedicarboxylate) and copolyesters comprising two or more of the above monomer repeat units.

[0068] In one aspect of the invention, articles are produced using the blend material (with or without fillers) via injection and rotational molding, resin film infusion, resin transfer molding, filament winding, powder coating to create a prepreg or film, hot melt prepreg preparation, compression molding, roll wrapping, water slurry, and pultrusion with or in some cases without reinforcement. The only proviso is that conditions allow for the polymerization of the blend to form high molecular weight polyester upon heating. Generally, most of such processes require that the resin to be processed have a low melt viscosity; therefore, conventional thermoplastic resins that have high melt viscosity are not suitable for processing. However, macrocyclic polyester oligomers have low melt viscosity.

[0069] Also, in processing conventional thermoplastic resins with such processes, the cooling of the mold after processing is required to solidify the melt. Demolding can occur only after such a cooling step. This results in longer processing time and increased energy usage. However, macrocyclic poly(1,4-butylene terephthalate) oligomers, for instance, polymerize at a temperature, from about 180°C to about 200°C, that is lower than the melting point of the resulting polyester polymer which is about 220°C. In addition, poly(1,4-butylene terephthalate) has a favorable crystallization rate even at such temperatures. Thus, the resulting polyester polymer crystallizes without cooling the mold allowing polymerization and demolding to occur at the same temperature thereby reducing processing time and energy consumption.

[0070] In applying macrocyclic polyester oligomers to the processes described below, a fast crystallization of the resulting polyester polymer may be desirable. Depending on the nature of the macrocyclic polyester oligomers, the nature of the resulting polymer, and the polymerization process employed, fast crystallization may need to be induced by cooling the mold wherein the polymerization process occurred. For instance, in general, high molecular weight poly(1,4-butylene terephthalate) crystallizes fairly rapidly even at 180°C to 200°C while, in general, poly(ethylene terephthalate) requires cooling from such temperatures to achieve a favorable crystallization rate. In cases where the polyester polymers have a melting point higher than the polymerization temperature but does not crystallize at a favorable rate, agents, such as nucleating agents, which facilitate crystallization may be employed. In cases where the polyester polymers have a melting point lower than the polymerization temperature, cooling is needed to bring about crystallization of the resulting polyester polymer.

[0071] In one embodiment of each of the following processes involving a polymerization of a macrocyclic polyester oligomer, no cycling (i.e., cooling and heating) the tools (e.g., the mold and/or other equipment) after polymerization is complete, is conducted. In another embodiment of each of the following processes involving a polymerization of a macrocyclic polyester oligomer, some cooling is conducted.

[0072] The following general definitions may be helpful in understanding the various terms and expressions used in this specification and particularly in the processes described below.

“Wet-out” means a process to cause a physical state of good and sustained contact between a liquid substrate and a solid substrate such that no substantial amount of air or other gas is trapped between the liquid substrate and the solid substrate. “Fiber” means any material with slender, elongated structure such as polymer or natural fibers. The material can be fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers. Fibers may also be grouped to form a “tow” or “strand”. A “tow” or “strand” is a group of fibers together, or a bundle of fibers which are usually wound onto spools and may or may not be twisted. These tows or strands can be woven or knitted to form fabrics. A “tackifier” or “binder” is resin or glue used in small amounts to lightly hold fibers together. A “fiber preform” is an assembly of fiber tows and/or fabric held together in a desired shape. Generally, fiber preform fibers are dry and may be held together with various tackifiers. A “prepreg” is a fiber material such as carbon fiber, glass fiber, or other fiber, that has been impregnated with a resin material in sufficient volume as to provide the matrix of the composite, and such that the ratio of fiber to resin is closely controlled. The fiber configuration can be in tow form, woven or knitted into a fabric, or in a unidirectional tape. The stickiness that allows multiple uncured layers to stick to one another during assembly is known as “tack”. The ability of a layer of material to be formed to a complex shape before it is processed is known as “drape”.

**a. Rotational Molding**

[0073] Referring to FIG. 1, rotational molding is a process for making hollow thermoplastic articles, such as a wide variety of articles including fluid storage tanks, tractor fenders and large children’s toys. In one aspect of the invention, rotational molding is used to manufacture articles from a macrocyclic polyester oligomer. Typically, the process begins by placing a macrocyclic

polyester oligomer and a polymerization catalyst in a mold **110**. After closing the mold **110**, the mold is rotated about two axes **120**, **130** simultaneously so that the contents roll over the intended areas of the inside of the mold. Heat **140** is applied to melt the macrocyclic polyester oligomer and the polymerization catalyst. After the macrocyclic polyester oligomer and the polymerization catalyst are melted, the rotation continues until the content polymerizes and solidifies. The part is demolded while the tools are hot or after some cooling of the tools. The process can then be repeated with the same equipment to produce another thermoplastic part. The rotation rates about the axes are often controlled so that the orientation of the mold takes a long time to repeat. This provides a uniform coverage inside the mold. Heat can be applied in the form of external gas flames, but internal electrical mold heating can also be used. One type of mold is made of aluminum with a wall thickness of  $\frac{1}{4}$  of an inch. Fiber reinforced plastic can be used as well.

**[0074]** In one embodiment of the invention, a process for polymerizing a macrocyclic polyester oligomer includes providing a macrocyclic polyester oligomer, providing a polymerization catalyst (or in the case of a blend material, providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), loading the macrocyclic polyester oligomer and the polymerization catalyst (or in the case of a blend material, loading the blend material) into a mold having a chamber, rotating the mold along at least one axis, and heating the mold or otherwise to cause polymerization. In one embodiment, the process also includes the step of removing the resulting polymer while the resulting polymer is at substantially the same temperature of the polymerization and the resulting polymer solidifies into a solid at the polymerization temperature.

**[0075]** In one embodiment, the macrocyclic polyester oligomer and the polymerization catalyst (or the blend material) is fed into a cool mold. In another embodiment, the macrocyclic polyester oligomer and the polymerization catalyst (or the blend material) is fed into a hot mold with the temperature of the mold being substantially the same as the polymerization temperature. In one embodiment, the mold is not cooled before the start of the next processing round. In another embodiment, the mold temperature is cooled before the next round of processing. In one embodiment, the mold is rotated along one axis. In another embodiment, the mold is rotated along two or more axes.

[0076] In one embodiment, the macrocyclic polyester oligomer processed by rotational molding is a macrocyclic PBT oligomer. A macrocyclic PBT oligomer has a melting point at about 180°C, which is much lower than the melting point of polymerized PBT, which is about 220°C. As a result, the polymerized PBT solidifies and can be removed from the mold at approximately the temperature at which polymerization is conducted.

[0077] In another embodiment, the macrocyclic polyester oligomers are macrocyclic PBT/PET co-oligomers. Macrocyclic PBT/PET co-oligomers have a melting point at about 180°C, which is much lower than that of the polymerized PBT/PET. Polymerized PBT/PET melts at about 220°C to 240°C depending on the PBT/PET ratio. As a result, the polymerized PBT/PET crystallizes and can be removed from the mold at the temperature at which polymerization is conducted.

[0078] In one embodiment, a filler is placed into the mold in which it is mixed with the macrocyclic polyester oligomer and the polymerization catalyst. In another embodiment, a filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst before being placed in the mold. In yet another embodiment, a filler is part of the blend material.

#### **b. Resin Film Infusion**

[0079] Referring to FIG. 2, resin film infusion is a process for making plastic composite articles that are predominantly flat on one face and may have detailed features. An illustrative example of such articles is aircraft wing skins which are typically constructed of a composite made with carbon fiber and epoxy resin. In one aspect of the invention, resin film infusion is used to manufacture articles from macrocyclic polyester oligomers. A layer or film 210 of a macrocyclic polyester oligomer containing a polymerization catalyst is placed in a mold 220 that has a layer of dry fiber 230. The macrocyclic polyester oligomer layer or film 210 is placed between the layer of dry fiber 230 and the mold surface 240. The mold 220 is then heated to melt the macrocyclic polyester oligomer layer or film 210, which then infuses into the dry fiber layer 230, usually under a force created by a vacuum 260 on the other side of the dry fiber layer 230. A vacuum bag 270 may be used together with a seal 280 maintained between the vacuum bag 270 and the mold surface 240. After the completion of polymerization, the part is either demolded hot or after some cooling of the tools.

**[0080]** In one embodiment, a process for polymerizing a macrocyclic polyester oligomer includes providing a macrocyclic polyester oligomer, providing a polymerization catalyst (or, in the case of a blend material, providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), loading the macrocyclic polyester oligomer and the polymerization catalyst (or in the case of a blend material, loading the blend material) into a mold having a dry layer of fibrous material to form a layer between the dry layer of fibrous material and a surface of the mold, heating the mold to melt the macrocyclic polyester oligomer, forcing the macrocyclic polyester oligomer and the polymerization catalyst to infuse into the dry layer of fibrous material, and heating the mold or otherwise to cause polymerization of the macrocyclic polyester oligomer. In another embodiment, the infusion process is facilitated, for example, by a pressure generated from a vacuum bag. The resin layer could also be between the vacuum bag and the fiber layer. The resin layer does not have to go against the mold. Because the resin film of the macrocyclic polyester oligomer melts to a low viscosity liquid, infusion into a fiber is easily accomplished. In one embodiment, the process also includes the step of removing the resulting polymer while the resulting polymer is at substantially the same temperature of the polymerization and the resulting polymer solidifies into a solid at the polymerization temperature. In one embodiment, no cooling of the mold is conducted before demolding or before the start of the next round of processing with the mold. In another embodiment, some cooling of the mold is conducted before demolding or the start of the next round of processing.

**[0081]** In another embodiment, a filler is placed into the mold in which it is mixed with the macrocyclic polyester oligomer and the polymerization catalyst. In another embodiment, a filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst before being placed in the mold. In yet another embodiment, a filler is part of the blend material.

**[0082]** In one embodiment, a macrocyclic PBT oligomer is polymerized using the resin film infusion processes described here.

**[0083]** In one embodiment, a macrocyclic polyester oligomer powder prepreg is used instead of the fabric and resin layers. A powder prepreg in this case is a base material, usually fibrous, that has been impregnated with macrocyclic polyester oligomers in powder form before they are placed in the mold. In another embodiment, a prepreg, described in the next section, is used in a

resin film infusion process. A prepreg may be a unidirectional prepreg whereon the impregnated content is distributed along one direction.

[0084] Typically with resin film infusion processes, if the resin is a thermoset, additional heat is typically needed to solidify the resin before demolding. If the resin is a conventional thermoplastic, the material generally must be cooled to re-solidify the resin before demolding can take place. The high viscosity of melted conventional thermoplastic materials and poor infusion characteristics have, in the past, made resin film infusion processes suitable almost exclusively to thermoset. As just described, macrocyclic polyester oligomers can be processed using a resin film infusion process to produce a thermoplastic.

### c. Prepreg Processes

[0085] In one embodiment, a unidirectional prepreg is in the form of unidirectional prepreg tape which includes a sheet of fibers. The sheet of fibers is held in the sheet form because the fibers are impregnated with macrocyclic polyester oligomers that hold them together. Two primary methods are used to make unidirectional prepreps from macrocyclic polyester oligomers, solvent impregnation and hot melt.

[0086] Referring to FIG. 3, a solvent impregnation method is implemented by running fabric or fiber tow 305 through a solvent bath 310 containing a macrocyclic polyester oligomer and a polymerization catalyst. The concentration of macrocyclic polyester oligomer is typically 30% by weight. The solvent is used to reduce the viscosity, which allows easy wet-out of the fabric or fiber tow 305. The fabric or fiber tow 305, wetted with the macrocyclic polyester oligomer, the polymerization catalyst, and the solvent, is then transported to drying oven 315 wherein the solvent is flashed off. The macrocyclic polyester oligomer and the polymerization catalyst remain on the fabric or fiber tow 305. The fabric or fiber tow 305 may be heated at temperatures and for an amount of time that allows some or all of the solvent to flash off in order to control tack. The amount of tack reduces as more solvent is flashed off. Then, the paper sheet 320 is rolled together with the fabric or fiber tow 305 to form a prepreg with paper backing 325, completing the prepreg process.

[0087] In one embodiment, a process for impregnating a macrocyclic polyester oligomer and a polymerization catalyst to form a prepreg includes the steps of dissolving a macrocyclic polyester



oligomer and a polymerization catalyst (or in the case of a blend material, dissolving a blend material having a macrocyclic polyester oligomer and a polymerization catalyst) in a solvent to form a solution, contacting the solution with a fibrous base material, and removing the solvent. In another embodiment, the solvent is removed by heat. In one embodiment, the fibrous base material is a fiber tow. In another embodiment, a release paper backing is provided and placed adjacent the macrocyclic polyester oligomer and the polymerization catalyst.

**[0088]** In one embodiment, a macrocyclic polyester oligomer is incorporated into a unidirectional prepreg using a solvent process. In one embodiment, a process for impregnating a macrocyclic polyester oligomer includes dissolving a macrocyclic polyester oligomer and a polymerization catalyst (or in the case of a blend material, dissolving a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), combining the solution with a filler to form a mixture, applying the mixture to a base material, and removing the solvent.

**[0089]** Referring to FIG. 4, a hot-melt method starts with a release paper **405** that has been coated with a layer of a macrocyclic polyester oligomer and a polymerization catalyst to a specific thickness. The release paper **405** having the coating thereon is stored on a roll **410**. When combined with a fiber tow **415** that has been preheated, the macrocyclic polyester oligomer and the polymerization catalyst on the release paper **405** is brought into contact with the fiber tow **415** and is heated by a heating block **420** to reduce viscosity of the coating. Compaction rollers **425** drive the fiber tow **415** into the macrocyclic polyester oligomer coating layer forming a prepreg with a paper backing which is then rolled onto roller **430**.

**[0090]** In one embodiment, a process for impregnating a macrocyclic polyester oligomer and a polymerization catalyst to form a prepreg includes the steps of providing a release base material having thereon a macrocyclic polyester oligomer and a polymerization catalyst (or in the case of a blend material, providing a release base material having thereon a blend material having a macrocyclic polyester oligomer and a polymerization catalyst) and pressing the release base material against a fibrous material under heat. In one embodiment, a filler is also impregnated with the macrocyclic polyester oligomer and the polymerization catalyst. In one embodiment, the filler is part of a blend material to be impregnated. In one embodiment, the prepreg is made with tack. A macrocyclic polyester oligomer containing appropriate amount of a polymerization catalyst is thinly spread on non-stick substrate surface and melted with instant heating. The

molten macrocyclic polyester oligomer is then rapidly cooled to quench from crystallization, resulting in a soft pliable film that can be removed from the substrate surface. Macrocyclic polyester oligomers made with tack are used in many applications that are generally for thermosetting resins. Macrocyclic polyester oligomers with tack are processed like a thermoset while producing a thermoplastic product.

**[0091]** A unidirectional prepreg tape of conventional thermoplastic does not have tack or drape at room temperature, it must be heated when formed, and is difficult to use. Thermally quenched non-crystalline macrocyclic polyester oligomers are soft and sticky at ambient temperature. Illustrative examples of such macrocyclic polyester oligomers are macrocyclic poly(1,4-butylene terephthalate) (PBT), poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), poly(ethylene terephthalate) (PET), and poly(1,2-ethylene 2,6-naphthalendicarboxylate) (PEN) oligomers and copolyester oligomers comprising two or more of the above monomer repeat units. Such macrocyclic polyester oligomers are used in the creation of a thermoplastic prepreg with tack and drape.

**[0092]** In one embodiment, a macrocyclic PBT oligomer and a polymerization catalyst is impregnated by the processes described here.

#### **d. Pultrusion**

**[0093]** Referring to FIG. 5, pultrusion is a process for making fiber reinforced plastic composite parts and components with a constant linear cross-section such as rods, tubes and bars stock, whereby fiber reinforcements are combined with a resin material and pulled through a heated die. The fiber-reinforced composite parts exit the die in the desired shape. In one aspect of the invention, pultrusion processes are used to manufacture articles from macrocyclic polyester oligomers. A dry fiber tow or fabric **510** is first pulled by puller **550** through the liquid resin bath **520** to apply the macrocyclic polyester oligomer and the polymerization catalyst **530**, and then is pulled by a puller **550** into the heated die **540** to polymerize the macrocyclic polyester oligomer, and to form the desired shape and to solidify. The viscosity of the liquid resin is relatively low, approximately 100's of centipoise at room temperature, and easily wets and impregnates the fiber material.

[0094] Variations of the above process include pumping the macrocyclic polyester oligomer and the polymerization catalyst into the die to completely eliminate the liquid resin bath. This process is sometimes called "Continuous Resin Transfer Molding" (CRTM). As to the fiber, it can be carbon, glass, aramid, or other fibrous materials.

[0095] In one embodiment of the invention, a pultrusion process is used to polymerize macrocyclic polyester oligomers for the manufacture of a variety of articles. Such a process includes providing a macrocyclic polyester oligomer, providing a polymerization catalyst (or in the case of a blend material, providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), pulling a fibrous strand into an elongated die, moving the macrocyclic polyester oligomer and the polymerization catalyst (or in the case of a blend material, moving the blend material) into the die thereby causing contact with and around the fibrous strand, heating to cause polymerization of the macrocyclic polyester oligomer forming high molecular weight polyester resin matrix around the fibrous strand, and pulling the polyester matrix into an exit portion of the die having a desired cross section thereby forming a rigid article. When the die is not heated to the melting point of the resulting polyester resin matrix and the crystallization rate of the resulting polymer is favorable at the polymerization temperature, no cooling is necessary to allow the solidification of the polyester resin matrix. In one embodiment, no cooling of the tools is conducted. In another embodiment, some cooling is conducted. In one embodiment, a blend material is injected directly into the pultrusion die. In one embodiment, a powder impregnation process, such as electrostatic powder coating, is used to combine the blend material with fiber strands prior to its introduction into the pultrusion die. In one embodiment, the process of combining the blend material and fiber strands is done off-line before pultrusion, and wound onto spools. In another embodiment, combination is done inline in place of the resin bath.

[0096] In another embodiment, the blend material in powder form is fed directly into the pultrusion die having a melting and impregnation zone. In another embodiment, the blend material is continuously melted outside the die, and pumped into the die in liquid form. In one embodiment, macrocyclic PBT oligomer is polymerized using the pultrusion processes described here.

[0097] Referring to FIG. 6, in one embodiment, macrocyclic polyester oligomers are used in a pultrusion process wherein the blend material is continuously melted outside the die and pumped into the die in liquid form. The blend material powder 610 is fed into hopper 620. An extruder 630 which has a barrel chamber with a rotating worm screw forces the powder into a heated zone 640 which is typically heated by an electricity, steam or oil system 650. The melted blend material exits the end of the extruder 660 and enters the pultrusion die. This process may also be adopted to employ a macrocyclic polyester oligomer and a polymerization catalyst not in the form of a blend material.

[0098] Referring to FIG. 7, in another embodiment of the invention, the blend material is continuously melted outside the die and pumped into the die in liquid form. A piston 710 is placed inside cool cylinder 720 and is connected to and driven by a ram 730. The blend material 735 is placed inside the cool cylinder between the front surface 740 of the piston 710 and the back surface 750 of the hot melting block 760. A hole in the melting block 765 allows the blend material to be pushed through the melting block 760. The hot melting block is typically heated by an electricity, steam or oil heating system 775. As the piston is pushed up, the blend material becomes melted as it comes into contact with the melting block 760, forms a melted region 780, and travels through a hole 765 in the melting block, out the exit from the melting head 790 and into the mold or pultrusion die. This process may also be adopted to employ a macrocyclic polyester oligomer and a polymerization catalyst not in the form of a blend material.

[0099] Generally, it is difficult to use conventional thermoplastic resins in the above processes because conventional thermoplastic resins are difficult to process due to their high melt viscosity. Macrocyclic polyester oligomers, however, melt to a low viscosity liquid. Low viscosity makes it easy to wet out fibers, like thermoset resins. Macrocyclic polyester oligomers can polymerize to high molecular weight thermoplastics. An additional advantage of using PBT-based macrocyclic polyester oligomers is that they will melt, wet out a fiber, polymerize, and crystallize or solidify all at a constant temperature, in the range of about 180°C to about 200°C. This reduces and even eliminates the need to cool the exit end of the pultrusion die, allowing the shortening of the die and/or the increase of the pull speed.

**e. Resin Transfer Molding**

**[0100]** Referring to FIG. 8, resin transfer molding is a process for making plastic composite articles in a variety of shapes and sizes, often with a smooth surface finish and requiring little or no additional trimming or machining, such as automotive body panels and chassis components, bicycle forks, and tennis rackets. In one aspect of the invention, resin transfer molding processes are used to manufacture articles from macrocyclic polyester oligomers. Generally, resin transfer molding begins with a fiber preform **810** that is close to the final shape of the part. The preform **810** is placed in a mold **820** of the desired final shape, and the mold is closed. A mixture of macrocyclic polyester oligomer and a polymerization catalyst is melted to a melt **830** that is then pumped in. The melt wets out the fiber preform **810** and fills any remaining volume **850**. Once the resulting polyester thermoplastic polymer solidifies the part is demolded. Depending on the nature of the macrocyclic polyester oligomers, the nature of the resulting polyester polymer, and the polymerization process, a cooling step may or may not be needed to bring about crystallization.

**[0101]** The melt **830** is usually injected slowly so that it wicks into the fiber of the fiber preform **810**. Vacuum applied to the vent **870** before and during processing can help eliminate trapped air. The vent **870** can also be sealed and the mold pressurized with resin to eliminate voids. Also, the mold can be heated to maintain the low viscosity of the resin and to effect polymerization. Resin transfer molding processes described here may be used to manufacture articles from macrocyclic polyester oligomers.

**[0102]** In one embodiment of the invention, a process for polymerizing a macrocyclic polyester oligomer includes providing a macrocyclic polyester oligomer, providing a polymerization catalyst (or in the case of a blend material, providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), loading the macrocyclic polyester oligomer and the polymerization catalyst (or loading the blend material) into the mold having the fibrous preform therein, heating the mold to melt the macrocyclic polyester oligomer, forcing the macrocyclic polyester oligomer and the polymerization catalyst into the fibrous preform, and heating the mold to cause polymerization of the macrocyclic polyester oligomer. In one embodiment, the process also includes the step of removing the resulting polymer while the resulting polymer is at substantially the same temperature of the polymerization and the resulting

polymer solidifies into a solid at the polymerization temperature. In one embodiment, no cooling of the mold is conducted before demolding or before the start of the next round of processing with the mold. In another embodiment, some cooling of the mold is conducted before demolding or the start of the next round of processing. In one embodiment, a macrocyclic PBT oligomer is polymerized using the resin film infusion processes described here. In another embodiment, no fibrous preform is used. Resin transfer molding can be done without a preform. Such a process is referred to as casting.

[0103] In another embodiment, a filler is placed into the mold in which it is mixed with the macrocyclic polyester oligomer and the polymerization catalyst. In another embodiment, a filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst before being placed in the mold. In yet another embodiment, a filler is part of the blend material as described above.

[0104] Because macrocyclic polyester oligomers melt to a low viscosity liquid, infusion into fibers is easily accomplished. After polymerization is complete, the part is demolded with or without cooling depending on the macrocyclic polyester oligomer employed, the nature of the resulting polyester polymer, and the polymerization process. Furthermore, resin transfer molding generally uses only thermosetting resins, such as epoxy, unsaturated polyester, and phenolic resins. In one embodiment, thermoplastic articles are manufactured from macrocyclic polyester oligomers using the resin transfer molding processes.

#### **f. Filament Winding**

[0105] Referring to FIG. 9, filament winding is a process for making plastic composite parts that are hollow and require high strength and light weight such as tubes, compressed air tanks, fluid storage tanks, and automotive drive shafts. In one aspect of the invention, filament winding processes are used to manufacture articles from macrocyclic polyester oligomers. Generally, the process involves the winding of fibers 910 onto a mandrel 920. One embodiment for loading a macrocyclic polyester oligomer and a polymerization catalyst is to simply brush them onto the mandrel 920 and wind the fibers 910 as the mandrel 920 rotates. Another embodiment is to use a resin bath, such as a dip tank or rollers, to impregnate the fibers 910 somewhere between the fiber spool 940 and the mandrel 920. Another embodiment is using a prepreg fiber tow with the

macrocyclic polyester oligomer and the polymerization catalyst in the tow to begin with. In another embodiment, the fibers are wound dry, followed by vacuum infusing with resin.

[0106] A macrocyclic polyester oligomers and a polymerization catalyst can be used in the form of a prepreg. Flat fiber bundle impregnated with a macrocyclic polyester oligomer and a polymerization catalyst is applied with heat and pressure at the location where the tape first touches the part. In one embodiment, the part is cool, and only the local vicinity around the tape contact is heated. A roller is typically used to apply the pressure to press the tape into the part and consolidate the material. The part can be wound cool. It can be removed from the mandrel immediately after winding. Some post heating and consolidation can be done to improve the properties of the part. In one embodiment, the blend material is pre-impregnated in a fiber tow.

[0107] In one embodiment, a process for polymerizing a macrocyclic polyester oligomer includes providing a macrocyclic polyester oligomer, providing a polymerization catalyst (or in the case of a blend material, providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), heating to cause the macrocyclic polyester oligomer to melt, contacting the molten macrocyclic polyester oligomer and the polymerization catalyst with a fibrous strand, winding the fibrous strand onto a mandrel, and heating the macrocyclic polyester oligomer to cause its polymerization. In one embodiment, the process also includes the step of removing the resulting polymer while the resulting polymer is at substantially the same temperature of the polymerization and the resulting polymer solidifies into a solid at the polymerization temperature. In one embodiment, no cooling of the mold is conducted before demolding or before the start of the next round of processing with the mold. In another embodiment, some cooling of the mold is conducted before demolding or the start of the next round of processing. In one embodiment, a macrocyclic PBT oligomer is polymerized using the resin film infusion processes described here.

[0108] In another embodiment, a filler is placed into the mold in which the filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst. In another embodiment, a filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst before being placed in the mold. In yet another embodiment, a filler is part of the blend material.

**g. Compression Molding**

[0109] Referring to FIG. 10, compression molding, stamping, or pressing, is a process for making plastic composite parts that are thin and generally flat with mild features and contours such as truck and auto body panels, bumper beams, various trays and machine housings. In one aspect of the invention, compression molding is used to manufacture articles from macrocyclic polyester oligomers. A press 1010 has a press frame 1020. Within the press 1010 are top die 1030 and lower die 1040. A prepreg or sheet molding compound (SMC) 1050 is placed between the top die 1030 and the lower die 1040 within the press 1010. The prepreg or molding compound 1050 typically is heated and stamped under heat and pressure and then removed. A SMC or sheet molding compound refers to a highly filled compound with a resin binder that is placed in a hot matched metal tool and compressed to evenly fill the mold and solidify into a net or near net shape part.

[0110] In one embodiment of the invention, a macrocyclic polyester oligomer is polymerized using compression molding. In one embodiment, a process for polymerizing a macrocyclic polyester oligomer includes providing a macrocyclic polyester oligomer, providing a polymerization catalyst (or in the case of a blend material, providing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst), providing a fibrous base material, heating to cause the macrocyclic polyester oligomer to melt, and loading the molten macrocyclic polyester oligomer and the polymerization catalyst onto the fibrous base material, pressing the dies of the mold, and heating or otherwise to cause polymerization of the macrocyclic polyester oligomer. In one embodiment, the process also includes the step of removing the resulting polymer while the resulting polymer is at substantially the same temperature of the polymerization and the resulting polymer solidifies into a solid at the polymerization temperature. In one embodiment, no cooling of the mold is conducted before demolding or before the start of the next round of processing with the mold. In another embodiment, some cooling of the mold is conducted before demolding or the start of the next round of processing.

[0111] In another embodiment, a filler is placed into the mold in which it is mixed with the macrocyclic polyester oligomer and the polymerization catalyst. In another embodiment, a filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst before being placed in the mold. In yet another embodiment, a filler is part of the blend material.



[0112] In one embodiment, a macrocyclic PBT oligomer is polymerized using the resin film infusion processes described here. In the case of PBT, the cycle time can be greatly reduced because the processing temperature is below the melting point of the resulting PBT polymer. In one embodiment, macrocyclic polyester oligomers are used to make high quality thermoplastic composite parts with powder coated fabric.

#### **h. Roll wrapping**

[0113] Referring to FIG. 11, roll wrapping is a process for making tubular articles such as composite golf shafts, windsurfing masts and various tie rods for aircraft. In one aspect of the invention, roll wrapping processes are used to manufacture articles from macrocyclic polyester oligomers. The tubular articles can be round, elliptical, or even rectangular cross sections. They can be tapered as well. A mandrel 1110 that serves as the forming core is placed on the edge 1120 of a layer of prepreg sheet 1130. The prepreg sheet 1130 is rolled onto the mandrel 1110. Proper tack on the prepreg sheet 1130 allows the mandrel 1110 to pick up the prepreg sheet 1130 to begin the wrapping process, and to allow the layers to adhere to one another. The fiber orientation 1140 may be alternated in a sequence of layers, so as to distribute strength as desired. The assembly can be wrapped tightly in shrink-wrap tape that shrinks when heated to apply pressure to the composite as it consolidates. In one embodiment, the assembly is heated to cause polymerization. In one embodiment, a macrocyclic polyester oligomer and a polymerization catalyst is impregnated in a sheet of reinforcing fibers to form the prepreg. The tack allows multiple uncured layers to stick to one another during assembly, and the drape allows the uncured sheet to be easily contoured to the shape of the component. Illustrative examples of such macrocyclic polyester oligomers are macrocyclic poly (1,4-butylene terephthalate) (PBT), poly(1,3-propylene terephthalate) (PPT), poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), poly(ethylene terephthalate) (PET), and poly(1,2-ethylene 2,6-naphthalendicarboxylate) (PEN) oligomers and copolyester oligomers comprising two or more of the above monomer repeat units.

[0114] In one embodiment, a process for polymerizing a macrocyclic polyester oligomer includes rolling onto a mandrel a base material having thereon pre-impregnated a macrocyclic polyester oligomer and a polymerization catalyst (or in the case of a blend material, a blend

material having a macrocyclic polyester oligomer and a polymerization catalyst), and heating or otherwise to cause polymerization of the macrocyclic polyester oligomer. In one embodiment, the blend material as described above is impregnated in a unidirectional prepreg and is processed by a roll wrapping process. In one embodiment, the process also includes the step of removing the resulting polymer while the resulting polymer is at substantially the same temperature of the polymerization and the resulting polymer solidifies into a solid at the polymerization temperature. In one embodiment, no cooling of the mold is conducted before demolding or before the start of the next round of processing with the mold. In another embodiment, some cooling of the mold is conducted before demolding or the start of the next round of processing. In one embodiment, a macrocyclic poly(1,4-butylene terephthalate) oligomer is polymerized using the resin film infusion processes described here.

[0115] In another embodiment, a filler is also pre-impregnated. In another embodiment, a filler is mixed with the macrocyclic polyester oligomer and the polymerization catalyst before being impregnated onto the base material. In yet another embodiment, a filler is part of the blend material having a macrocyclic polyester oligomer and a polymerization catalyst.

#### **i. Powder Coating**

[0116] Another type of prepreg is powder coating. Powder coatings are done through electrostatic or other processes. Referring to FIG. 12, an electrostatic powder coating involves placing a powder 1205 in a chamber 1210 that has tiny holes 1215 in the bottom 1220 that air (or other gases) are forced through. As the gas passes through the powder it begins to bubble and flow like a fluid; this is known as a fluidized bed 1225. The powder particles in the fluidized bed 1225 can then be charged electrostatically forming charged resin particles 1227 and will adhere electrostatically, upon heating at a heating zone 1229, to a solid substrate that passes through the charged fluidized powder, such as a fiber tow or fabric 1230. The fiber tow or fabric is then brought to roll onto a roller 1240.

[0117] In another embodiment, charged powder particles are sprayed through a nozzle. The powder particles adhere electrostatically to the solid substrate used to receive them. In one embodiment, charged powder particles are sprayed using an electrostatic powder spraying technique. In one embodiment, the powder is stored in a reservoir with caking being prevented

by slow stirring with an agitator. In another embodiment, air fluidization of the bed is used as an alternative to mechanical stirring. The powder is conveyed to the electrostatic spray head by air motion. In one embodiment, the spray head is fastened onto a gun-like holder for convenience of operation. An orifice is fitted onto the spray head. Before the powder particles leave the orifice, they are electrostatically charged by internal electrodes connected to a high-tension generator. The target substrate to be sprayed with the powder is attached to an electrically grounded holder. The powder is projected towards the target by the flow of air. The target is electrically grounded so that the powder particles will adhere during subsequent operations where the sprayed sheets must be handled. The thickness of the powder layer laid down by the electrostatic spraying technique is primarily a function of the total charge of powder deposited on the target, which in turn is a function of the voltage applied.

[0118] In one embodiment, powder coating is used to deposit a uniform coating of a powder material onto a receiving substrate. Illustrative examples of receiving substrates include paper, metals, plastics, carbon, glass, and aramid fibers. The receiving substrate is usually moving in a continuous process. The powder is heated or treated in other ways to make the powder adhere to or soak into the receiving substrate. Thermoset resin powders are currently applied to a variety of fibrous materials to make preregs or coatings for paper or metals. Thermoplastic powders are used to create preregs in an attempt to get a better connection between the reinforcing fibers and thermoplastic matrix. Still, even powder coated thermoplastic preregs are difficult to use because conventional thermoplastic materials have high melt viscosity and do not wet out fibers well and have long heat up and cool down cycles when making parts. Thus, conventional thermoplastic materials are difficult to use to produce high quality composites.

[0119] In one embodiment, a blend material containing a macrocyclic polyester oligomer and a polymerization catalyst is used in a powder coating system, for example, in an electrostatic powder coating process. The macrocyclic polyester oligomer is slightly melted to adhere to the fiber and used as a prepreg in an uncured state. Such a prepreg is then processed under heat and pressure to allow the resin to flow and polymerize to produce high quality composites with good surface finish and fiber wet out. The low melt viscosity of macrocyclic polyester oligomers make them process like a thermoset although they can produce thermoplastics.

**j. Water Slurry Process**

**[0120]** Preparation of prepregs from solid polymer precursors and substrate fibers can be conducted by a number of methods as mentioned above. Often, the impregnation process needs to be conducted under a limited time/temperature process window to avoid premature curing of the resin. While the use of organic solvents allows a process to be performed under a wider ranges of time and temperature, the cost associated with solvent recovery and environmental control may be problematic.

**[0121]** An aqueous suspension or slurry of polymers or polymer-precursors can be used to coat fiber substrates to prepare pre-impregnated sheets for production of fiber-reinforced composites. Many vinyl polymers are available in aqueous forms produced by emulsion or suspension polymerization. However, such aqueous systems are generally not available for polycondensation polymers and their precursors. Typically, when a solid powder of a macrocyclic polyester oligomer is combined with water, it does not mix well because of a large difference in surface energy between the solid particles and water. The addition of a water-miscible organic solvent such as methanol, ethanol, iso-propanol, acetone, etc., can help the macrocyclic polyester oligomer or the polymerization catalyst to dissolve. This may, however, result in the generation of environmentally undesirable volatile organic compounds (VOCs). On the other hand, use of aqueous suspension of the resin is inherently low cost and avoids the use of VOCs. Macrocyclic polyester oligomers such as macrocyclic poly(1,4-butylene terephthalate) oligomer (macrocyclic PBT oligomer) can be prepared into a stable aqueous mixture or, more preferably, a suspension with the aid of a trace amount of various surfactants.

**[0122]** As used here, a “suspension” means a fluid containing homogeneously suspended fine particles, depending on the physical appearance such as thickness it may also be called a slurry or simply a mixture. A “slurry” means a fluid containing fine powders suspended with the help of surfactants. A “mixture” means a fluid containing liquid mixed with fine powders.

*Making a Water Suspension or Slurry*

**[0123]** The water slurry process can be used to manufacture articles from macrocyclic polyester oligomers. In one embodiment, a process for preparing a suspension of a macrocyclic polyester oligomer and a polymerization catalyst includes contacting the macrocyclic polyester oligomer

and the polymerization catalyst with water and a surfactant and mixing the macrocyclic polyester oligomer and the polymerization catalyst with water and the surfactant thereby producing a suspension.

[0124] The step of mixing may be accomplished by any means so long as the resulting mixture is a suspension. Any physical mixing procedures that achieve a suspension may be employed. Therefore, conventional means of mixing, for example, mechanical agitation, sonication, and continuous circulation by pumping, may be employed. Such physical mixing may be facilitated by the addition of chemicals. Other illustrative examples of such processes include milling, solvent process followed by evaporation, etc. Solvents other than water may be added to facilitate the mixing, further processing, or both. In one embodiment, a solvent other than water is used to produce a suspension of macrocyclic polyester oligomers. For example, an organic solvent such as methylene chloride or ethyl alcohol may be employed. However, as mentioned above, this may result in the generation of VOCs. In a preferred embodiment, no solvent other than water is employed to produce a suspension of the macrocyclic polyester oligomer and the polymerization catalyst in water. Furthermore, the mixture may contain additional components such as a filler and other additives. Illustrative additives include colorants, pigments, filler, reinforcing fibers, magnetic materials, anti-oxidants, UV stabilizers, plasticizers, fire-retardants, lubricants, mold releases, etc.

[0125] In one embodiment, a small amount of a nonvolatile surfactant is employed to facilitate suspension formation and to increase suspension stability. In one embodiment, less than 2 weight percent of surfactant is employed. In another embodiment, less than 1 weight percent of surfactant is employed. In another embodiment, less than 0.05 weight percent of surfactant is employed. Commercially available surfactants are typically not volatile. The quantity that is required to facilitate suspension formation may be negligible in causing environmental effect. In the presence of a surfactant, wetting of solid powder is greatly facilitated. Typically, the resulting suspension is more stable, avoiding rapid settlement of the solid on standing. In one embodiment, the suspension is produced by milling a macrocyclic polyester oligomer and a polymerization catalyst in the presence of water and a surfactant.

[0126] Any surfactant that facilitates aqueous suspension formation and does not adversely interfere with the polymerization and the resulting polymerization products may be employed. In

one embodiment, only one surfactant is employed. In another embodiment, two or more surfactants are employed. In one embodiment, a nonionic surfactant, such as, polyethylene glycol monoalkyl ether, is employed. In another embodiment, an ionic surfactant is employed. Ionic surfactants provide for added stability of the suspension by introducing surface electrical charges on dispersed solid particles. In one embodiment, an anionic surfactant is employed. Illustrative examples of anionic surfactants include sodium dodecylbenzenesulfonate, which is a common laundry detergent component, and sodium dodecyl sulfate. In another embodiment, a cationic surfactant is employed. Illustrative examples of cationic surfactants include dodecylpyridinium chloride, dodecyltrimethylammonium bromide, dodecyltriphenylphosphonium bromide, coco and tallow-based quaternary ammonium salts, and 1-octadecyl-3-methylimidazolium bromide. In one embodiment, a surfactant that carries both a positive and a negative charge in the same molecule is employed. In one embodiment, a surfactant containing glycerin and sugar moieties as a polar group is employed. Surfactants containing glycerin and sugar moieties as a polar group may be advantageously employed to introduce branching and cross-linking in the final polymer.

[0127] The stability of suspensions depends on factors including particle size, concentration of solid, concentration of surfactant, etc. Typically, the smaller the particle size, the more stable is the resulting suspension. In one embodiment, a process for achieving small particle suspension is to mill the macrocyclic polyester oligomer with water and a surfactant. One advantage of this process is that it eliminates the potential problem of handling fine particle dust.

[0128] Certain polymerization catalysts, including many tin catalysts, pre-inoculated with the macrocyclic polyester oligomer were essentially not affected despite the presence of water and the surfactant during the suspension forming process. As described below, such catalysts are effective in catalyzing polymerization after the removal of water.

#### *Prepreg Formation and Polymerization of MPOs*

[0129] One embodiment of a prepreg formation process is depicted in FIG. 13. Fibers 1310 are released from the fiber rolls 1320 and are arranged into desired width, usually that of the prepreg to be produced. The fibers 1310 are then pulled into a bath 1330 that contains a water suspension or slurry 1340 of a macrocyclic polyester oligomer, a polymerization catalyst, and a

surfactant, with or without additional filler or solvent. The fibers 1310 then are pulled into a drying oven 1350 wherein water is dried off. The fibers 1310 are then pulled into a fuse die 1360 that is heated to melt the macrocyclic polyester oligomer onto the fibers 1310. Depending on the die temperature and the rest time of the fibers 1310 in the fuse die 1360, the macrocyclic polyester oligomer may polymerize in the fuse die 1360. The fibers 1310 then go into a chill die 1370 to cool down. The prepreg is collected onto a drum 1380. The temperatures and hold times can be configured such that the MPOs fully or partially polymerize in the fuse die, or they can be polymerized later.

[0130] FIG. 14 shows another embodiment of a process that may be employed to make preregs of a macrocyclic polyester oligomer, to polymerize a macrocyclic polyester oligomer, or both. Generally, the process involves a suspension 1410 of water, a macrocyclic polyester oligomer, a polymerization catalyst, and a surfactant, with or without additional filler or solvent. The suspension is applied through a funnel 1415 to a base material 1420 to form a layer 1430 of the mixture on the base material 1420. The layer 1430 of the suspension is heated to remove water from the suspension. Once dry, the remaining suspension is then pressed into a desired form between belts 1440 run by rollers 1450. The resulting prepreg may be left un-polymerized and partially consolidated or may be fully polymerized and consolidated (or some combination) depending on whether additional heating is applied after the drying step to cause polymerization of the macrocyclic polyester oligomer.

[0131] In one embodiment, a process for impregnating macrocyclic polyester oligomers for polymerization includes providing a suspension of a macrocyclic polyester oligomer and a polymerization catalyst in water, applying the suspension to a base material, drying the applied suspension to remove water, and pressing the dried applied suspension to a desired form.

[0132] The step of providing a suspension of a macrocyclic polyester oligomer and a polymerization catalyst in water is discussed above.

[0133] Applying the suspension to a base material may be accomplished by any means so long as the suspension contacts a receiving base material and forms thereon a layer of the suspension of a desired shape and thickness. Depending on the application, the thickness and/or shape of the layer of the applied suspension may not be important and, therefore, not monitored or controlled. Illustrative examples of methods for applying the suspension include dropping the suspension

through a funnel with an appropriately sized and shaped opening and the use of a container that can be tilted or otherwise causing its content to spill over to the receiving base material. If it is useful to closely monitor and control the shape, thickness, and features of the resulted layer, additional devices may be included in the equipment to provide such monitoring or control.

**[0134]** The receiving base material may or may not become, after the water slurry process, part of the resulting prepreg or the partially or completely polymerized product. The base material may be a sheet of a polymer film or a paper coated with polymer film. The base material may be the surface of a portion of the processing equipment itself. The base material, if not to become a part of the prepreg or the polymerized product, may be removed after the step of applying the suspension and before the end of the water slurry process. Furthermore, the base material may include raised boundaries that help to contain the suspension and/or to achieve a certain shape, thickness, or features.

**[0135]** After applying the suspension to a base material, the applied suspension may be dried by any method so long as it results in the removal of water from the applied suspension. Illustrative examples of the methods for drying the applied suspension include heating, drying by blowing or bubbling a hot gas through or over the suspension, drying through a vacuum, or a combination of all or some of these or other methods. A component (other than water) of the applied suspension (e.g., a solvent such as ethyl alcohol) may be removed before further processing. The method used for removing water may be helpful or even sufficient in removing certain solvents. Thus, an additional step may or may not be needed. Depending on the nature of the component(s) to be removed, a removal step may be carried out before, during, or after the step of applying the suspension. As indicated above, VOCs are preferably avoided.

**[0136]** Pressing may be accomplished by any means so long as the desired form results. A desired form may include certain shape, thickness, and features. Thus, vacuum forming, double rolling, and/or a die may be used in shaping the product into the desired form. In applications in which polymerization is carried out, pressing may be conducted before, during, or after polymerization. Also, pressing may or may not apply to the base material depending on the application. Similarly, the base material, if it is to be removed, may be removed before, during, or after pressing. Furthermore, pressing may not be needed in certain applications where the



form of the prepreg or polymerized product need not be controlled or may be achieved by the other steps of the water slurry process.

[0137] Depending on the application, immediate polymerization of the macrocyclic polyester oligomer may or may not be desired. If it is desired, polymerization may be achieved by heating the applied suspension to a temperature sufficient to cause polymerization of the macrocyclic polyester oligomer. In one embodiment, heating is not employed and drying is achieved by other methods with no polymerization resulting from the drying step. In another embodiment, heating is employed to achieve drying but not to cause polymerization. In another embodiment, heating results in drying the suspension and partial polymerization of the macrocyclic polyester oligomer. In yet another embodiment, heating results in complete polymerization of the macrocyclic polyester oligomer.

[0138] In one embodiment, a double belt press system is employed in preparing preregs from a macrocyclic polyester oligomer and a polymerization catalyst, with or without additional fillers. Referring to FIG. 14 again, the layer 1430 comprising a macrocyclic polyester oligomer and a polymerization catalyst, with or without additional fillers, is pressed between belts 1440 run by rollers 1450. The belts 1440 move with the layer 1430 while the layer 1430 is being pressed, heated, or both. Therefore, the temperature and period of heating may be configured such that the layer 1430 is fully polymerized, partially polymerized, or not polymerized. Similarly, the temperature and period of heating or cooling may be configured to achieve full or partial consolidation. The heat history may include any combination of heating step(s) and cooling step(s) in order to achieve the desired heat history. The material of layer 1430 may be a melt or a solid or a combination of the two along the way of the double belt press depending on the specific configurations of the temperature, the timing, and the pressure.

[0139] While FIG. 14 shows a double belt press system in the context of the water slurry process, applicability of the double belt press system is not limited to the water slurry process. The double belt press system can be used to prepare preregs from macrocyclic polyester oligomers alone or in combination with other processes described herein to achieve the desirable preregs.

[0140] In one embodiment, the polymerization catalyst present in the suspension is from 0.01 to 10.0 mole percent of the structural repeat units of the macrocyclic polyester oligomer. The

polymerization catalysts that may be employed are as discussed above. In one embodiment, the process includes the additional step of heating the dried applied suspension to cause polymerization of the macrocyclic polyester oligomer. In one embodiment, a suspension of a macrocyclic polyester oligomer and a polymerization catalyst in water is provided using the process for making a water suspension or slurry described above.

**[0141]** A cooling step may or may not be needed depending on the application. In cases where cooling is not necessary, such as where drying is accomplished by methods other than heating and where no polymerization is carried out, the prepreg or product can be removed or demolded from the equipment soon after the water slurry process. If cooling is necessary, demolding can be carried out after the desired temperature has been achieved.

**[0142]** In one embodiment, the material processed by the above process includes a blend material. In one embodiment, a blend material containing a macrocyclic polyester oligomer and a polymerization catalyst is mixed with water and processed by a water slurry process. In one embodiment, the blend material further contains a filler.

**[0143]** In one embodiment, a macrocyclic polyester oligomer composition includes a macrocyclic polyester oligomer, a polymerization catalyst, and water. In one embodiment, the macrocyclic polyester oligomer composition further includes a surfactant. In one embodiment, the macrocyclic polyester oligomer composition further includes a filler and other additives such as pigments, mold releases and stabilizers. In one embodiment, a polyester polymer composite is prepared by drying the macrocyclic polyester oligomer composition followed by polymerization of the macrocyclic polyester oligomer.

**[0144]** In one embodiment, a process for impregnating a macrocyclic polyester oligomer for polymerization and for polymerizing a macrocyclic polyester oligomer includes mixing a blend material comprising a macrocyclic polyester oligomer and a polymerization catalyst with water with or without a surfactant to form a mixture, applying the mixture to a base material, drying the mixture to remove water, and pressing the dried mixture to form a prepreg.

**[0145]** In one embodiment, the blend material further includes a filler. In one embodiment, a polyester polymer composite is prepared by polymerizing a macrocyclic polyester oligomer according to the above process. In one embodiment, an article of manufacture is produced by the above process.

[0146] For certain applications, it may be desirable to form a suspension that can last for a long period of time without any components precipitating out of the suspension before the step of applying the mixture. For other applications, a suspension may be formed and substantial uniformity within the suspension kept by agitation and/or stirring before and during the step of applying the mixture.

[0147] In order to properly carry out the water slurry process and other processes described above, grinding may be necessary to reduce macrocyclic polyester oligomers into a powder form. Typically, macrocyclic polyester oligomers have a low molecular weight and can be ground into fine powder easily at ambient temperature thereby reducing the cost of material. Conventional thermoplastics like nylon and polypropylene are not as easy to grind at ambient temperature and need to be cooled or frozen. Certain conventional thermoplastics require very low (cryogenic) temperatures to make grinding possible thereby dramatically increasing the cost of material.

[0148] The success of a water slurry process in prepreg formation and polymerization of macrocyclic polyester oligomers was unexpected partly because the presence of water, in general, disrupts and can even entirely prevent the polymerization process from starting and progressing. Once the water is removed by drying, however, the polymerization process can take place uninterrupted. The water slurry process thus provides an effective and relatively inexpensive method for preparing prepreg and polymer from macrocyclic polyester oligomers.

## V. Examples

[0149] The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention. The products obtained from these examples may be confirmed by conventional techniques such as proton and carbon-13 nuclear magnetic resonance spectroscopy, mass spectroscopy, infrared spectroscopy, differential scanning calorimetry and gel permeation chromatography analyses.

### *Example A*

[0150] The macrocyclic polyester oligomers used in the following example are macrocyclic copolyester oligomers with 95.0 mol% of PBT and 5.0 mol% of PET. The macrocyclic copolyester oligomers were prepared by heating a mixture of copolyester linears, organic

solvents, such as *o*-xylene and *o*-dichlorobenzene, which are substantially free of oxygen and water, and tin or titanium compounds as transesterification catalysts.

[0151] A clean stainless steel reactor equipped with a magnetically coupled stirrer and heater with controls was charged with 4800 ml (4176 grams) of *o*-xylene, 59.2 grams (0.269 moles) of PBT pellets and 2.72 grams (0.0142 moles) of PET pellets to produce a 0.06 M polymer/*o*-xylene solution. The solution was heated to 100°C and sparged with dry nitrogen until the moisture content of water was about 5 ppm. Sparging also removed the dissolved oxygen in the solvent and inerted the reactor. The reactor was then sealed. The mixture was heated to 220°C. After the temperature was stabilized, 3.5 mole% of catalyst, titanium butanediol (based on total moles of polyester monomer repeat units), were added to the system by pressure transferring the catalyst into the system with the aid of dry *o*-xylene (flushing the catalyst into the system to ensure complete transfer) and nitrogen. This marked time zero in the experiment. The resulting reaction mixture was sampled by removing 1-2 ml samples of the mixture periodically from the system using the system's pressure as the driving force and a small sintered filter placed in the system to provide the pressure drop to atmospheric conditions. The collected samples were analyzed by HPLC to determine yields of macrocyclic copolyester oligomers. After approximately one hour, the catalyst was quenched by the addition of water (0.20 mol) by adding the water in an *o*-xylene mixture. The water/*o*-xylene mixture was pressure transferred into the system, and the system was then allowed to cool to 75°C with stirring in progress. The resulting reacted mixture was then filtered through a heated filter. Filtration resulted in removal of precipitated linear impurities (carboxylic acid terminated linear oligomers) from the system. The filtrate that contained the desired macrocyclic copolyester oligomers (dissolved in *o*-xylene at 75°C) was then evaporated or roto-evaporated down to about 40 ml and then nonsolvent (pentane) was added to induce precipitation of the oligomers. The precipitated macrocyclic copolyester oligomers were filtered off and dried. Purity of the macrocyclic copolyester oligomers obtained was greater than 99%, indicated by no observable hydroxybutyl terminated linears in the product.

### ***Example 1***

[0152] Twenty milligrams of 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane ("stannoxane-1") was dissolved with heating in approximately 2.5 ml of toluene which had been

pre-dried by treating with 4A molecular sieves. The solution was cooled and poured into a glass jar containing 5.0 g of finely pulverized macrocyclic copolyester oligomer of PBT/PE (95/5 molar ratio). After intimately mixing the resulting uniform paste was dried under vacuum at about 50°C. The white crusty solid was pulverized by using a pestle and a mortar. The resulting uniform free flowing white powder contained 0.3 mole% of tin atoms per mole of the copolyester monomer repeat units.

#### *Example 2*

[0153] Example 1 was repeated except that 33.0 mg of stannoxane-1 catalyst was employed to give a blend containing 0.5 mole% of tin atoms per mole of the copolyester monomer repeat units.

#### *Example 3*

[0154] Di-n-butyltin oxide (24.89 g, 0.100 mole), 2,2-diethyl-1,3-propanediol (13.22 g, 0.100 mole) and 75 ml of toluene were placed in a 250 ml, three necked flask equipped with a Dean-Stark condenser. The mixture was stirred under nitrogen and heated to reflux for approximately 2 hours during which time approximately 1.7 ml of water was separated. The Dean-Stark condenser was replaced with another Dean Stark condenser filled with molecular sieves. The reaction mixture was further heated to reflux for an additional hour and then approximately 60 ml of the toluene was distilled off. Upon cooling, a white crystalline solid was obtained. The yield of 1,1-di-n-butyl-4,4-diethyl-1-stanna-2,5-dioxacyclohexane ("stannoxane-2") was 36.1 g.

#### *Example 4*

[0155] Approximately one gram of the blend obtained in Example 1 was placed in a 25 ml round bottom flask and it was blanketed with nitrogen. The flask was then dipped in an oil bath maintained at 190°C. The powder completely melted in one minute to form an easy-to-flow colorless liquid. The viscosity of the liquid gradually increased within a period of 2 to 3 minutes and then started to solidify with crystallization, resulting in formation of a tough porcelain white solid. The polymerization was complete in 10 minutes.

### **Examples 5**

[0156] Stannoxane-2 (26 mg, 0.0727 mmol) was dissolved in 2 g of dry toluene. The solution was added to 4.0 g of the macrocyclic copolyester oligomers obtained in Example A in a jar. The content was mixed to form a homogeneous white paste. The paste was dried under vacuum in an oven at approximately 50°C. The crusty solid blend obtained was ground to obtain uniform powder containing 0.4 mole % tin atoms per mole of the copolyester monomer repeat units.

### **Example 6**

[0157] Example 5 was repeated except that 13 mg of stannoxane-2 catalyst was used to give a blend containing 0.2 mole % tin atoms per mole of the copolyester monomer repeat units.

### **Example 7**

[0158] Example 5 was repeated except that 6.5 mg of stannoxane-2 catalyst was used to give a blend containing 0.1 mole % tin atoms per mole of the copolyester monomer repeat units.

### **Examples 8-10**

[0159] Blend materials obtained in Examples 5-7 were subjected to test polymerization. One hundred milligrams of each sample were placed in a one-gram screw-cap vial. The vial was capped under nitrogen. The vial was then dipped in a 190°C oil bath. The blend melted in 50-60 seconds to form a colorless fluid. Table 2 shows the times taken to show marked viscosity increase and to observe a porcelain-white solid following crystallization.

**Table 2.** Polymerization of the blends

	Stannoxane-2 Conc. (mol%)	Time to show Viscosity increase (min)	Start of crystallization (min)
Example 8	0.4	1.5	4.5
Example 9	0.2	2	6
Example 10	0.1	10	18

### **Example 11 (Pultrusion 1, glass ribbon)**

[0160] Pultrusion was done using one end of FGI (Fiber Glass Industries), 113 yd/lb yield, standard sizing "Flexstrand" fiberglass roving, and was pulled at a rate of 12 inch/min, first

through a preheating die at 200°C (4 inch long, ½ inch x 0.025 inch cross section). The blend powder obtained in Example 1 was then placed on the fibers as they entered a tapered die (4 inch long, ½ inch x 0.070 inch at the entrance, and ½ inch x 0.015 inch at the exit) that was heated to 200°C. The powder melted and polymerized in the die (polymerization indicated by (1) molecular weight of 50k obtained from GPC analysis, and (2) the apparently high flexural strength as compared to that of the uncatalyzed macrocyclic oligomers which is extremely low), and exited in a molten but highly viscous state, followed by rapid crystallization within 2 inches of the die, indicated by a visual change from clear to opaque (light tan in color).

**Example 12** (Pultrusion 2, carbon ribbon)

[0161] This example is the same as Example 11 except that the fiberglass is replaced with Zoltek, 413 ft/lb yield, X-10 sizing, 48k filament count, carbon fiber. The resulting ribbon also displayed good mechanical strength, and the resulting polymer had molecular weight of 50k based on GPC analysis.

**Example 13** (Pultrusion 3, glass rod)

[0162] This example was run at 15 inch/min pull rate, used 3 strands of FGI, 113 yd/lb yield, standard sizing "Flexstrand" fiberglass roving, with a preheated die at 200°C. The blend material (in powder form) obtained in Example 1 was placed on the fibers as they entered a tapered, round die heated to 200°C (0.25 inch diameter at the entrance, reducing to 0.125 inch at 1 inch from the entrance, and a constant 0.125 inch diameter for the remaining 7 inch of the 8 inch long die). The resulting rod was substantially structural. The resulting polymer had a molecular weight of 50k based on GPC analysis.

**Example 14** (Unidirectional prepreg)

[0163] One gram of macrocyclic PBT oligomer blend material with stannoxane-1 catalyst is dissolved in 2 grams of methylene chloride (about 66% by weight of solvent), and combined with about 1 gram of carbon fiber on a plastic sheet. After the solvent flashed off, the sample was dry and looked powdery. The powder did not flake off during handling. The prepreg was then processed in a press, compression molding, at about 20 psi for 3 minutes at about 200°C using Teflon sheets. The resulting sheet was significantly structural.

**Example 15 (Compression molding)**

[0164] Four layers of dry, 5.7 oz./square yard carbon fabric were used with cyclic PBT blend material spread over the surface, at a fiber to resin weight ratio of 2:1. The layers with coating ("the sample") was placed in a heated platen press, at a temperature of about 190°C, and held at low pressure (less than 5 psi) for 3 minutes. The sample was then pressed at 200 psi for an additional 17 minutes. The sample was removed hot, i.e., without cooling the press. The sample was crystallized and firm.

**Example 16 (Water slurry)**

[0165] A blend material of macrocyclic PBT oligomer was prepared by the process of Example 1, using the catalyst of stannoxane-1. The blend material was ground to fine powder. The blend material was then mixed with water and/or ethyl alcohol to create a slurry. The mixture was allowed to remain in suspension for at least 24 hours. The material was then heated to remove water and further heated to cause polymerization of the macrocyclic PBT oligomer. The polymerization results are listed in Table 3.

**Table 3. Water Slurry Process Results (PBT/[Stannoxane-1])**

Test Id.	Components of mixture in equal weight	Mixture Description	Mw	% Conversion <sup>a</sup>
a	macrocyclic PBT, Ethyl alcohol	miscible	126,030	Medium <sup>b</sup>
b	macrocyclic PBT, Ethyl alcohol, water	miscible	147,300	High <sup>b</sup>
c	macrocyclic PBT (control)	n/a	155,722	High <sup>b</sup>
d	macrocyclic PBT, water	suspension	146,698	High <sup>b</sup>

<sup>a</sup> - % Conversion is from macrocyclic poly(1,4-butylene terephthalate) oligomer to linear polymer.

<sup>b</sup> - High = 95-100%; Medium = 90-95%; Low = less than 90%.

[0166] The procedure was then repeated except that the catalyst in the blend material was different. The catalyst used here was commercially available butyltin dihydroxide chloride (FASCAT™4101 from Atochem). The polymerization results are listed in Table 4.



**Table 4. Water Slurry Process Results (PBT/[FASCAT™4101])**

Test Id.	Components of mixture in equal weight	Mixture Description	Mw	% Conversion <sup>a</sup>
e	macrocyclic PBT, Ethyl alcohol	miscible	79,439	Medium <sup>b</sup>
f	macrocyclic PBT, Ethyl alcohol, water	miscible	91,669	Medium <sup>b</sup>
g	macrocyclic PBT (control)	n/a	126,539	High <sup>b</sup>
h	macrocyclic PBT, water	suspension	108,213	Medium <sup>b</sup>

<sup>a</sup> - % Conversion is from macrocyclic poly(1,4-butylene terephthalate) oligomer to linear polymer.

<sup>b</sup> - High = 95-100%; Medium = 90-95%; Low = less than 90%.

**Example 17 (Water slurry prepreg)**

[0167] A blend material of macrocyclic PBT oligomer was prepared by the process of Example 1, using the catalyst of stannoxane-1. The blend material was ground to fine powder. The blend material was then mixed with water and/or ethyl alcohol to create a slurry. The mixture was allowed to remain in suspension for at least 24 hours. Unsized AS4 type carbon fiber was then dipped into the slurry and removed with a slurry coating. The coated fiber was then dried under vacuum for 30 minutes at 80°C to form the prepreg. The prepreg was cut into ½ inch pieces, stacked randomly between steel sheets, wrapped in aluminum foil, dried again under vacuum for 30 minutes at 80°C, and pressed at 190°C for 30 minutes, to make a composite plate. The polymerization result for the resin in the plate is given in Table 5.

**Table 5. Water Slurry Prepreg Process Results (PBT/[Stannoxane-1])**

Test Id.	Mw	% Conversion <sup>a</sup>
JEG1	136,000	High <sup>b</sup>

<sup>a</sup> - % Conversion is from macrocyclic poly(1,4-butylene terephthalate) oligomer to linear polymer.

<sup>b</sup> - High = 95-100%; Medium = 90-95%; Low = less than 90%.

[0168] The procedure was then repeated except that the catalyst in the blend material was different. The catalyst used here was FASCAT™4101. The polymerization result for the resin in the plate is given in Table 6.

**Table 6. Water Slurry Prepreg Process Results (PBT/[FASCAT™4101])**

Test Id.	Mw	% Conversion <sup>a</sup>
JEG2	115,000	High <sup>b</sup>

<sup>a</sup> - % Conversion is from macrocyclic poly(1,4-butylene terephthalate) oligomer to linear polymer.

<sup>b</sup> - High = 95-100%; Medium = 90-95%; Low = less than 90%.

**Example 18** (Water slurry)

**[0169]** The cyclic oligomer employed was a macrocyclic co-polyester oligomer (c-PBT) with 95mol% poly(butylene terephthalate) repeat units and 5 mol% of poly(ethylene terephthalate) repeat units. Two types of the blend material were formulated. The first blend of macrocyclic c-PBT oligomer contained homogeneously distributed stannoxane-1. The concentration of the catalyst was 0.3 mol% of tin atom based on total moles of monomer repeat units. The second blend contained 0.4 mol% of FASCAT™4101.

(1) General procedure for making aqueous suspension

**[0170]** Nine grams of macrocyclic c-PBT oligomer blend containing a polymerization catalyst, 21 ml of water, and a surfactant as indicated were placed in a 100 ml screw-cap glass bottle along with five 7/16" stainless steel balls. The tightly capped bottle was then tumbled for 2 hours. A stable white milky suspension was obtained.

(2) Polymerization

**[0171]** Approximately 5.4 g of the aqueous suspension were spread on the bottom of a 100 ml beaker and it was dried at 60°C under vacuum in an oven. The dried solid powder (0.20g) was then placed in a 5 ml test tube. A vacuum was applied and the test tube was immersed in a 190°C oil bath. The macrocyclic c-PBT oligomer melted to form a fluid liquid during a period of 2 min after which heating was continued under argon atmosphere. Total polymerization time was 20 min for samples containing 0.3 mol% of stannoxane-1 and 30 min for samples containing 0.4 mol% of FASCAT™4101.

**[0172]** Results from samples containing an anionic surfactant, various cationic surfactants, and a non-ionic surfactant are summarized in Tables 7, 8, and 9, respectively.

**Table 7. Suspensions Prepared with Anionic Surfactant**

Sample	Polym. Catalyst (mol%)	Surfactant <sup>a</sup> (ppm)	Suspension Drying Cond.	Polym. time	Conv (%)	M <sub>p</sub> <sup>b</sup> (10 <sup>3</sup> )
Control	Stannoxane-1 (0.3)	Original powder, not suspension		20 min	97.8	140.6
i	Stannoxane-1 (0.3)	NaDBS (50)	60°C/vacuum	20 min	93.6	131.2
j	Stannoxane-1 (0.3)	NaDBS (200)	60°C/vacuum	20 min	95.6	133.2
k	Stannoxane-1 (0.3)	NaDBS (200)	110~120°C/in air	20 min	91.0	130.4
l	Stannoxane-1 (0.3)	NaDBS (1000)	60°C/vacuum	20 min	92.9	125.3
m	FASCAT <sup>TM</sup> 4101 (0.4)	Original powder, not suspension		30 min	94.8	123.9
n	FASCAT <sup>TM</sup> 4101 (0.4)	NaDBS (200)	60°C/vacuum	30 min	94.8	114.0

<sup>a</sup>- NaDBS: Sodium dodecylbenzenesulfonate

<sup>b</sup>- Peak molecular weight determined by GPC.

**Table 8. Suspensions Prepared with Cationic Surfactants**

Sample	Polym. Catalyst (mol%)	Surfactant <sup>a</sup> (ppm)	Suspension Drying Cond.	Polym. time	Conv (%)	M <sub>p</sub> <sup>b</sup> (10 <sup>3</sup> )
o	Stannoxane-1 (0.3)	DPyr (200)	60°C/vacuum	20 min	93.1	131.9
p	Stannoxane-1 (0.3)	Im (200)	60°C/vacuum	20 min	94.4	134.8
q	Stannoxane-1 (0.3)	DTPP (200)	60°C/vacuum	20 min	95.2	136.8
r	Stannoxane-1 (0.3)	DTMAB (200)	60°C/vacuum	20 min	95.9	141.3
s	FASCAT <sup>TM</sup> 4101 (0.4)	DPyr (200)	60°C/vacuum	30 min	94.0	116.2

<sup>a</sup>- DPyr: Dodecylpyridinium chloride; Im: 1-Octadecyl-3-methylimidazolium bromide;

DTPP: Dodecyltriphenylphosphonium bromide; DTMAB: Dodecyltrimethylammonium bromide.

<sup>b</sup>- Peak molecular weight determined by GPC.

**Table 9. Suspension Prepared with Non-ionic Surfactant**

Sample	Polym. Catalyst (mol%)	Surfactant <sup>a</sup> (ppm)	Suspension drying	Polym. time	Conv (%)	M <sub>p</sub> <sup>b</sup> (10 <sup>3</sup> )
t	FASCAT <sup>TM</sup> 4101 (0.4)	Brij 30 <sup>tm</sup> (200)	60°C/vacuum	30 min	94.0	122.6

<sup>a</sup>- Brij 30: Tetra(ethylene glycol) monododecyl ether.

<sup>b</sup>- Peak molecular weight determined by GPC.

[0173] The chemical stability of the aqueous suspensions may vary depending on the environment and chemical nature of the components. Tables 10-11 show the effect of catalyst, surfactant, and polymerization time on the molecular weight of polyesters obtained.

**Table 10. Chemical Stability of Suspension-1**

Sample	Polym. Catalyst (mol%)	Surfactant <sup>a</sup> (ppm)	Suspension Time (at RT)	Polym. time	Conv (%)	M <sub>p</sub> <sup>b</sup> (10 <sup>3</sup> )
Control	FASCAT™ 4101 (0.4)	Original dry powder		30 min	94.8	123.9
Control	FASCAT™ 4101 (0.4)	Only H <sub>2</sub> O	2 h	30 min	93.1	123.9
u	FASCAT™ 4101 (0.4)	DPyr (200)	2 h	30 min	94.0	116.2
v	FASCAT™ 4101 (0.4)	DPyr (200)	11 days	30 min	89.4	100.1
w	FASCAT™ 4101 (0.4)	NaDBS (200)	2 h	30 min	94.8	114.0

<sup>a</sup>.- DPyr: Dodecylpyridinium chloride (cationic); NaDBS: Sodium dodecylbenzenesulfonate (anionic).

<sup>b</sup>.- Peak molecular weight determined by GPC.

**Table 11. Chemical Stability of Suspension-2**

Sample	Polym. Catalyst (mol%)	Surfactant <sup>a</sup> (ppm)	Suspension Time (at RT)	Polym. time	Conv (%)	M <sub>p</sub> <sup>b</sup> (10 <sup>3</sup> )
Control	Stannoxane-1 (0.3)	Original dry powder		20 min	97.8	140.6
Control	Stannoxane-1 (0.3)	Only H <sub>2</sub> O	2 h	20 min	~95	134.8
x	Stannoxane-1 (0.3)	DTMAB (200)	2 h	20 min	95.9	141.3
xx	Stannoxane-1 (0.3)	DTMAB (200)	12 days	20 min	97.5	137.8
y	Stannoxane-1 (0.3)	NaDBS (200)	2 h	20 min	93.4	138.7
yy	Stannoxane-1 (0.3)	NaDBS (200)	11 days	20 min	93.2	124.4

<sup>a</sup>.- DTMAB: Dodecyltrimethylammonium bromide (cationic); NaDBS: Sodium dodecylbenzenesulfonate (anionic).

<sup>b</sup>.- Peak molecular weight determined by GPC.

[0174] Each of the patent documents disclosed hereinabove is incorporated by reference herein. Variations, modifications, and other implementations of what is described herein will occur to those of ordinary skill in the art without departing from the spirit and the scope of the invention as claimed. Accordingly, the invention is to be defined not by the preceding illustrative description but instead by the spirit and scope of the following claims.

## CLAIMS

What is claimed is:

- 1 1. A process for preparing a suspension of a macrocyclic polyester oligomer and a  
2 polymerization catalyst in water, said process comprising the steps of  
3 (a) contacting said macrocyclic polyester oligomer and polymerization catalyst with  
4 water and a surfactant, and  
5 (b) mixing said macrocyclic polyester oligomer and polymerization catalyst with said  
6 water and said surfactant thereby forming a suspension.  
7
- 1 2. The process of claim 1 wherein step (a) comprises contacting said macrocyclic polyester  
2 oligomer and polymerization catalyst with water and a nonionic surfactant.  
3
- 1 3. The process of claim 2 wherein said nonionic surfactant is polyethylene glycol monoalkyl  
2 ether.  
3
- 1 4. The process of claim 1 wherein step (a) comprises contacting said macrocyclic polyester  
2 oligomer and polymerization catalyst with water and an anionic surfactant.  
3
- 1 5. The process of claim 4 wherein said anionic surfactant is sodium  
2 dodecylbenzenesulfonate.  
3
- 1 6. The process of claim 1 wherein step (a) comprises contacting said macrocyclic polyester  
2 oligomer and polymerization catalyst with water and a cationic surfactant.  
3
- 1 7. The process of claim 6 wherein said cationic surfactant is selected from a group  
2 consisting essentially of dodecylpyridinium chloride, dodecyltrimethylammonium  
3 bromide, dodecyltriphenylphosphonium bromide, and 1-octadecyl-3-  
4 methylimidazolinium bromide.

5

1 8. The process of claim 1 wherein step (a) comprises contacting said macrocyclic polyester  
2 oligomer and polymerization catalyst, water, a surfactant, with a solvent.

3

1 9. The process of claim 1 wherein step (a) comprises milling said polymeric material in the  
2 presence of water and a surfactant.

3

1 10. A process for impregnating macrocyclic polyester oligomers for polymerization  
2 comprising the steps of:

3 (a) providing a suspension of a macrocyclic polyester oligomer and a polymerization  
4 catalyst in water;

5 (b) applying said suspension to a base material;

6 (c) drying to remove water from said applied suspension; and

7 (d) pressing said dried applied suspension to a desired form.

8

1 11. The process of claim 10 wherein step (a) comprises providing a suspension of a  
2 macrocyclic polyester oligomer and a polymerization catalyst in water, and wherein said  
3 macrocyclic polyester oligomer and said polymerization catalyst are components of a  
4 blend material.

5

1 12. The process of claim 10 wherein step (a) comprises providing a suspension of a  
2 macrocyclic polyester oligomer and a polymerization catalyst in water, and wherein said  
3 polymerization catalyst is present in an amount from 0.01 to 10.0 mole percent of said  
4 structural repeat units of said macrocyclic polyester oligomer.

5

1 13. The process of claim 10 wherein step (a) comprises providing a suspension of a  
2 macrocyclic polyester oligomer and a polymerization catalyst in water, and wherein said  
3 macrocyclic polyester oligomer comprises at least one of a homo- and co-polyester  
4 oligomer.

5

- 1 14. The process of claim 10 wherein step (a) comprises providing a suspension of a  
2 macrocyclic polyester oligomer and a polymerization catalyst in water, and wherein said  
3 polymerization catalyst is a tin compound.  
4
- 1 15. The process of claim 10 wherein step (a) comprises providing a suspension of a  
2 macrocyclic polyester oligomer and a polymerization catalyst in water, and wherein said  
3 polymerization catalyst is a titanate compound.  
4
- 1 16. The process of claim 10 further comprising, after step (c), the step of heating said dried  
2 applied suspension to cause polymerization of said macrocyclic polyester oligomer.  
3
- 1 17. An article of manufacture comprising the polymerized applied mixture of claim 16.  
2
- 1 18. The process of claim 10 wherein step (c) comprises heating said applied mixture.  
2
- 1 19. A process for impregnating macrocyclic polyester oligomers for polymerization using the  
2 process of claim 1, said method comprising the steps of:  
3 (a) providing a suspension of a macrocyclic polyester oligomer and a polymerization  
4 catalyst in water by performing the process of claim 1;  
5 (b) applying said suspension to a base material;  
6 (c) drying to remove water from said applied suspension; and  
7 (d) pressing said dried applied suspension to a desired form.  
8
- 1 20. A composition of macrocyclic polyester oligomer comprising:  
2 (a) a macrocyclic polyester oligomer;  
3 (b) a polymerization catalyst; and  
4 (c) water.  
5
- 6 21. The composition of claim 20 further comprising a surfactant.  
7

1 22. The composition of claim 20 further comprising a filler.

2

1 23. A polyester polymer composite prepared by drying the composition of claim 20 and  
2 polymerizing said macrocyclic polyester oligomer.

3

1 24. An article of manufacture comprising said polyester polymer composite of claim 23.

2

1 25. A process for impregnating macrocyclic polyester oligomers for polymerization  
2 comprising the steps of:

3 (a) mixing a blend material comprising a macrocyclic polyester oligomer and a  
4 polymerization catalyst with water to form a mixture;

5 (b) applying said mixture to a base material;

6 (c) drying to remove water from said applied mixture;

7 (d) heating said dried applied mixture to polymerize said macrocyclic polyester  
8 oligomer; and

9 (e) pressing said polymerized applied mixture to a desired form.

10

1 26. A polyester polymer composite prepared by polymerizing said macrocyclic polyester  
2 oligomer of claim 25.

3

1 27. An article of manufacture comprising said polyester polymer composite of claim 26.

2



## A BLEND MATERIAL INCLUDING MACROCYCLIC POLYESTER OLIGOMERS AND PROCESSES FOR POLYMERIZING THE SAME

### Abstract of the Disclosure

A water slurry process is used to prepare a prepreg and to manufacture articles from macrocyclic polyester oligomers. In one embodiment, a process for preparing a water suspension of macrocyclic polyester oligomers includes the steps of contacting a macrocyclic polyester oligomer and a polymerization catalyst with water and a surfactant, and mixing the macrocyclic polyester oligomer and polymerization catalyst with water and the surfactant thereby forming a suspension. In another embodiment, a process for impregnating macrocyclic polyester oligomers for polymerization includes the steps of providing a suspension of a macrocyclic polyester oligomer and a polymerization catalyst in water, applying the suspension to a base material, drying to remove water from the suspension, and pressing the dried suspension to a desired form. In yet another embodiment, a composition of macrocyclic polyester oligomer includes a macrocyclic polyester oligomer, a polymerization catalyst, and water. In yet another embodiment, a process for polymerizing macrocyclic polyester oligomers includes the steps of mixing a blend material having a macrocyclic polyester oligomer and a polymerization catalyst with water to form a mixture, applying the mixture to a base material, drying to remove water, heating to polymerize the macrocyclic polyester oligomer, and pressing the polymerized macrocyclic polyester oligomer to a desired form.

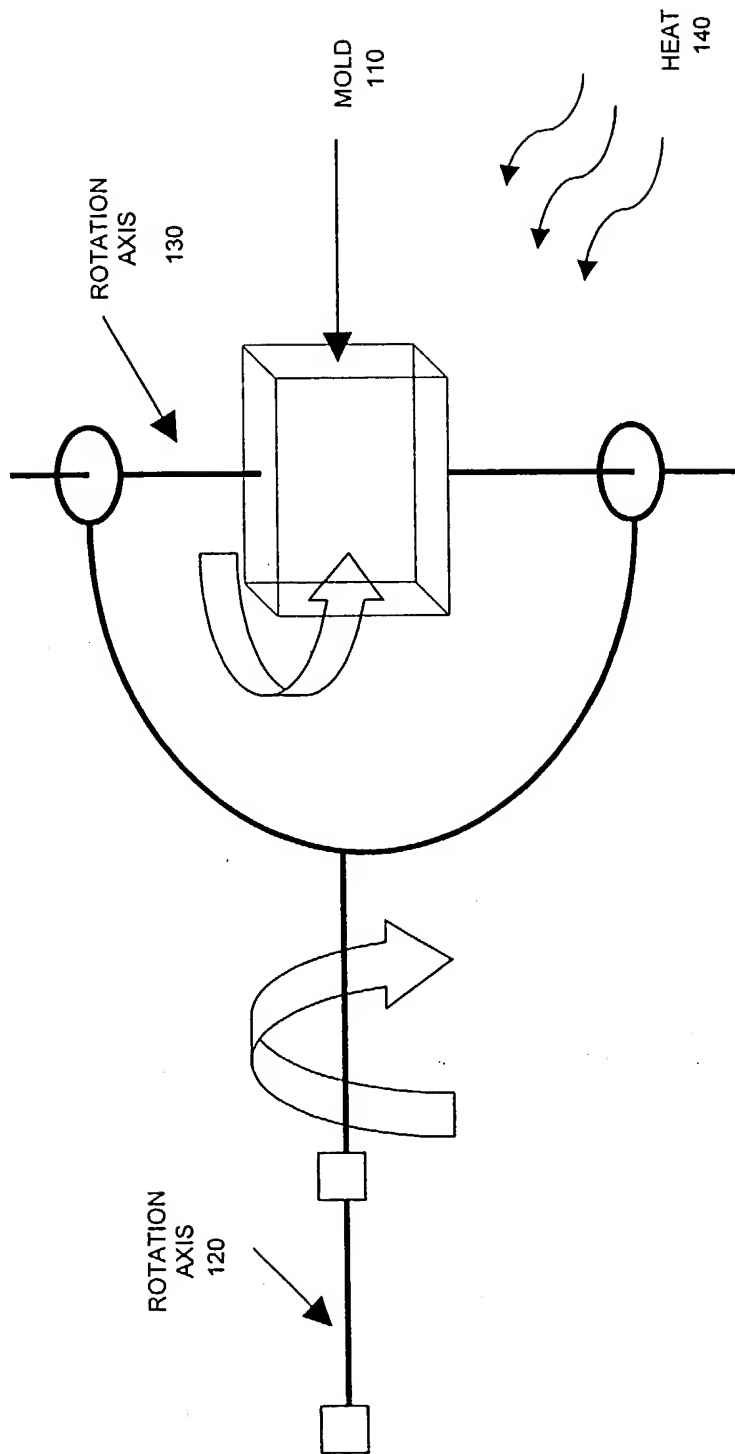


FIG. 1 ROTATIONAL MOLDING PROCESS

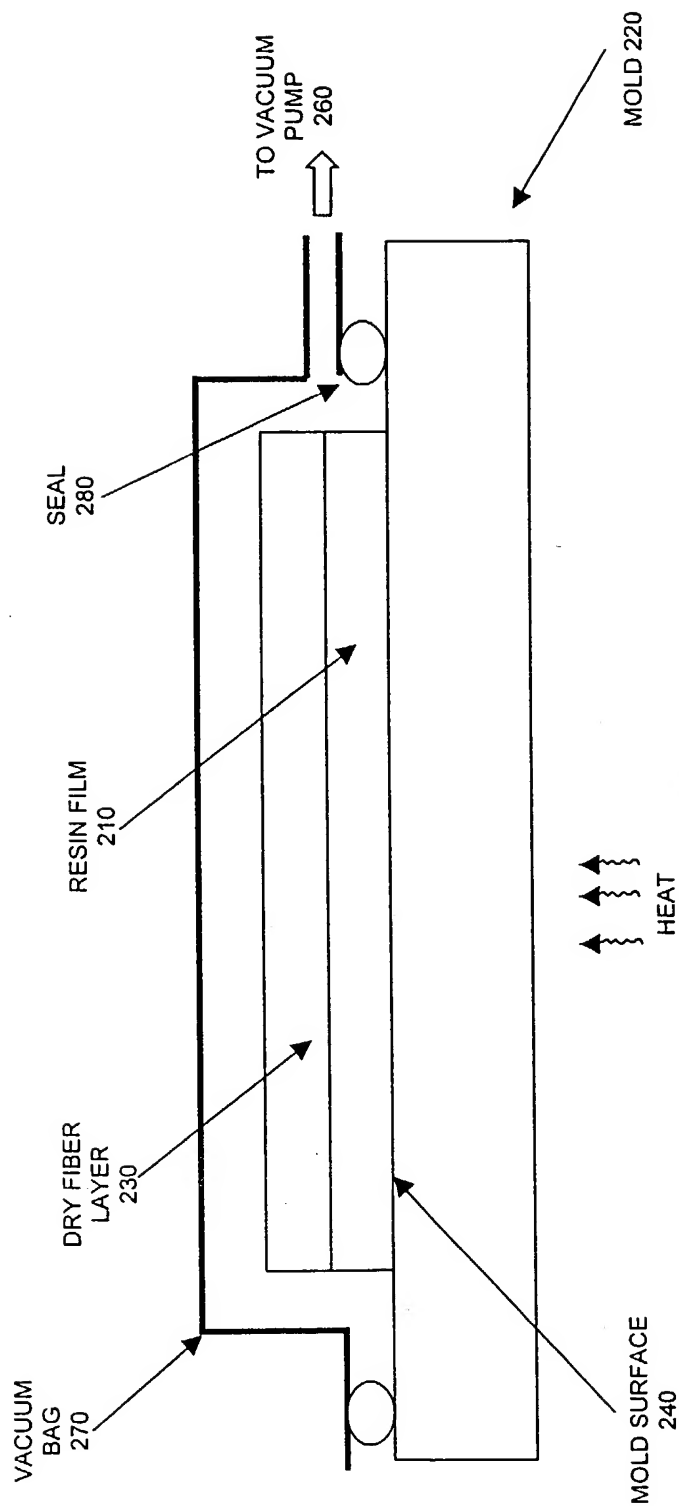


FIG. 2 RESIN FILM INFUSION PROCESS

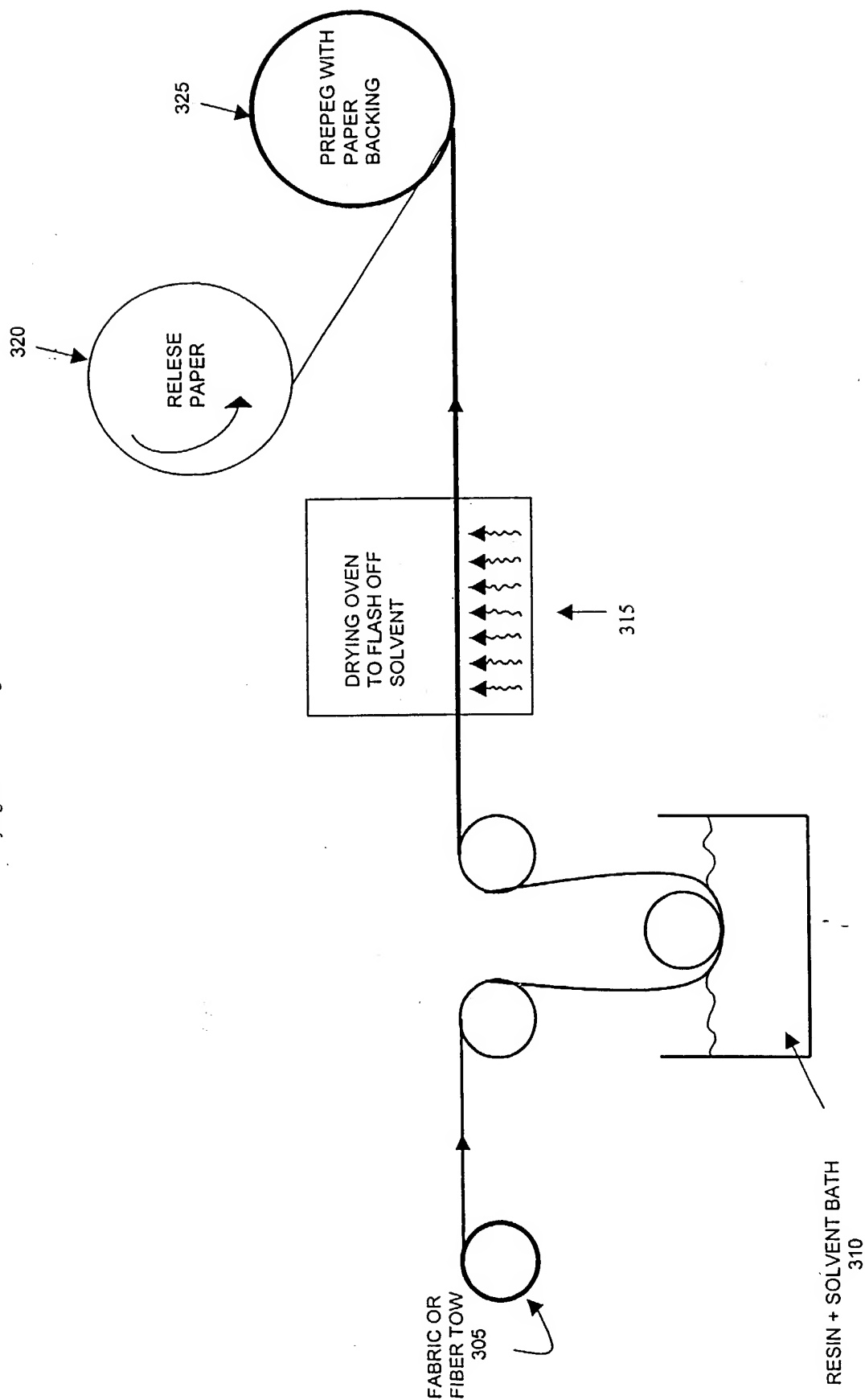


FIG. 3 SOLVENT PREPEG PROCESS

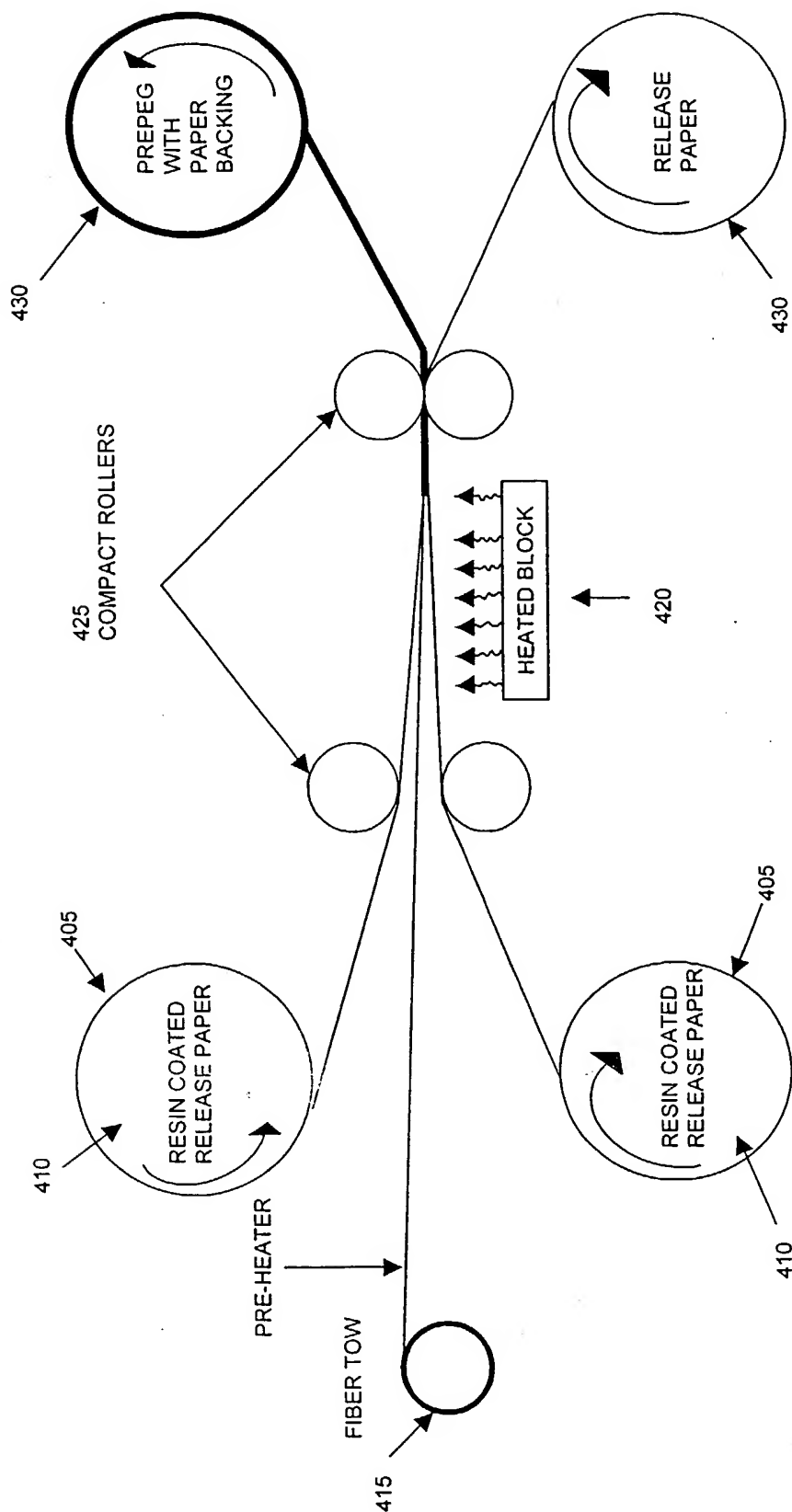


FIG. 4 HOT MELT PREPREG PROCESS

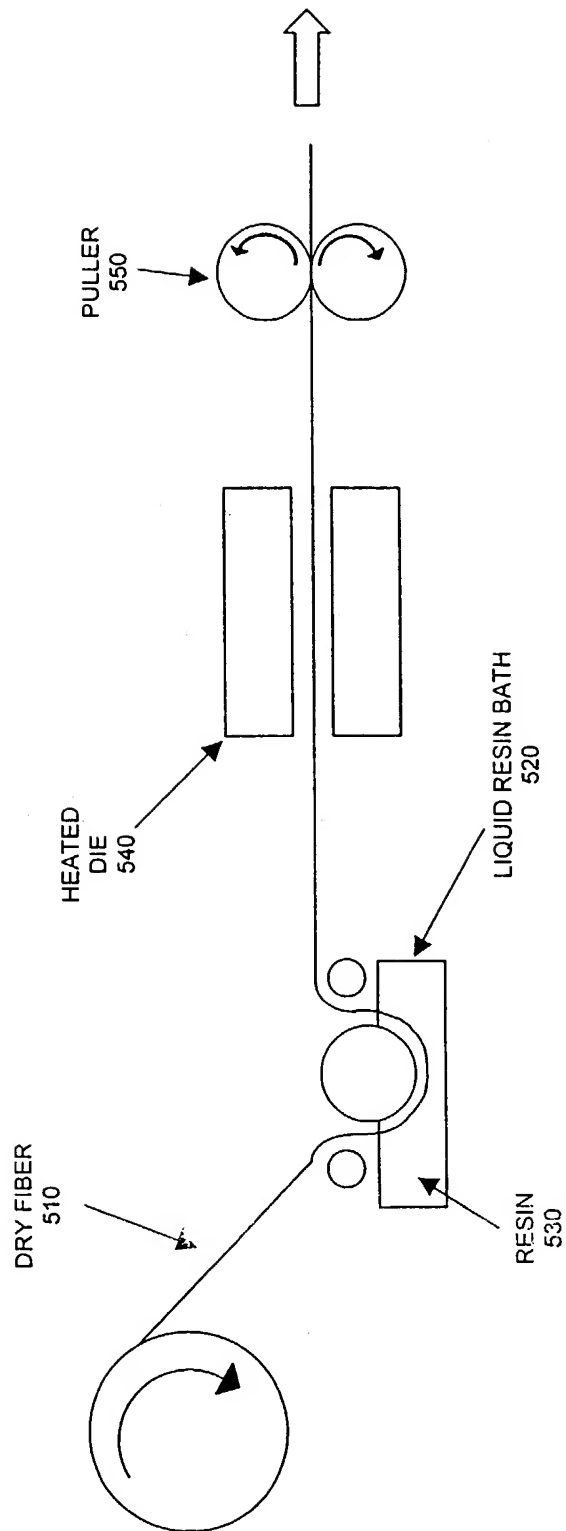


FIG. 5 PULTRUSION PROCESS

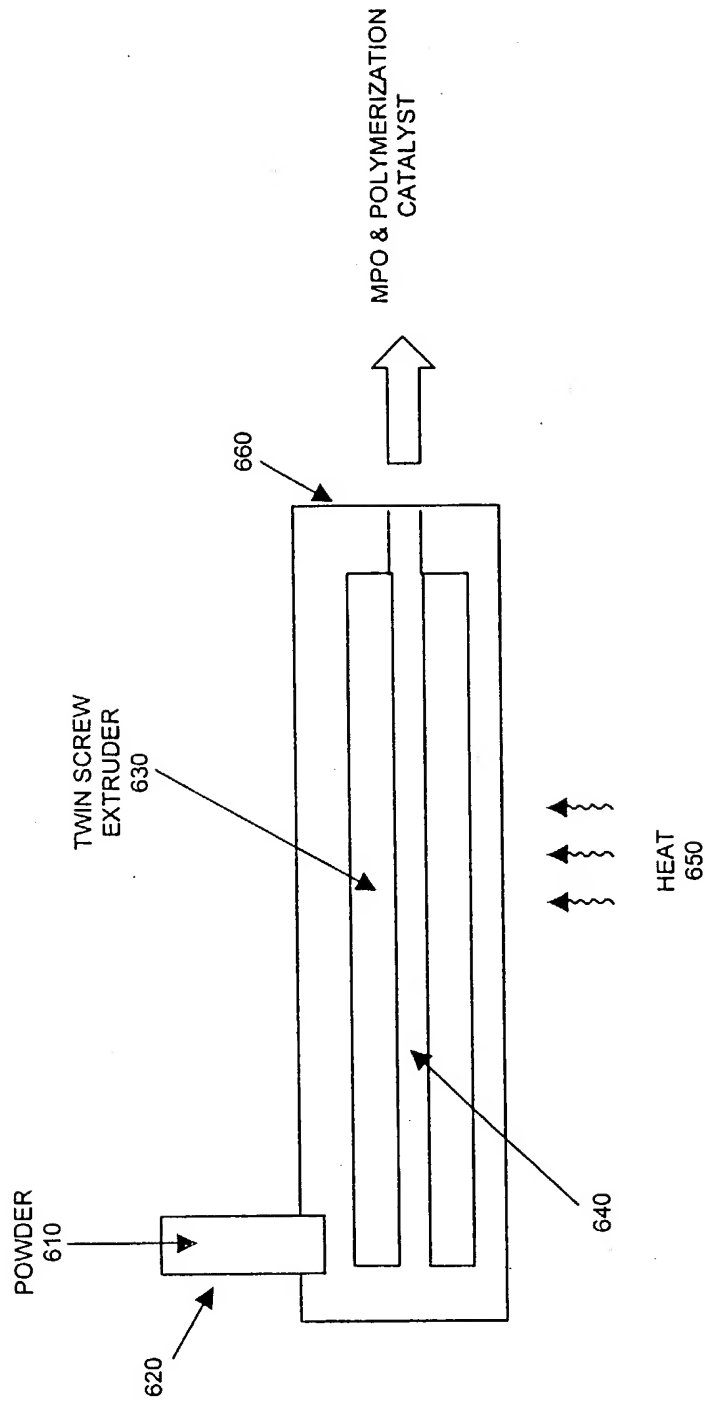


FIG. 6 TWIN SCREW EXTRUDER FOR MELTING  
THE BLEND MATERIAL

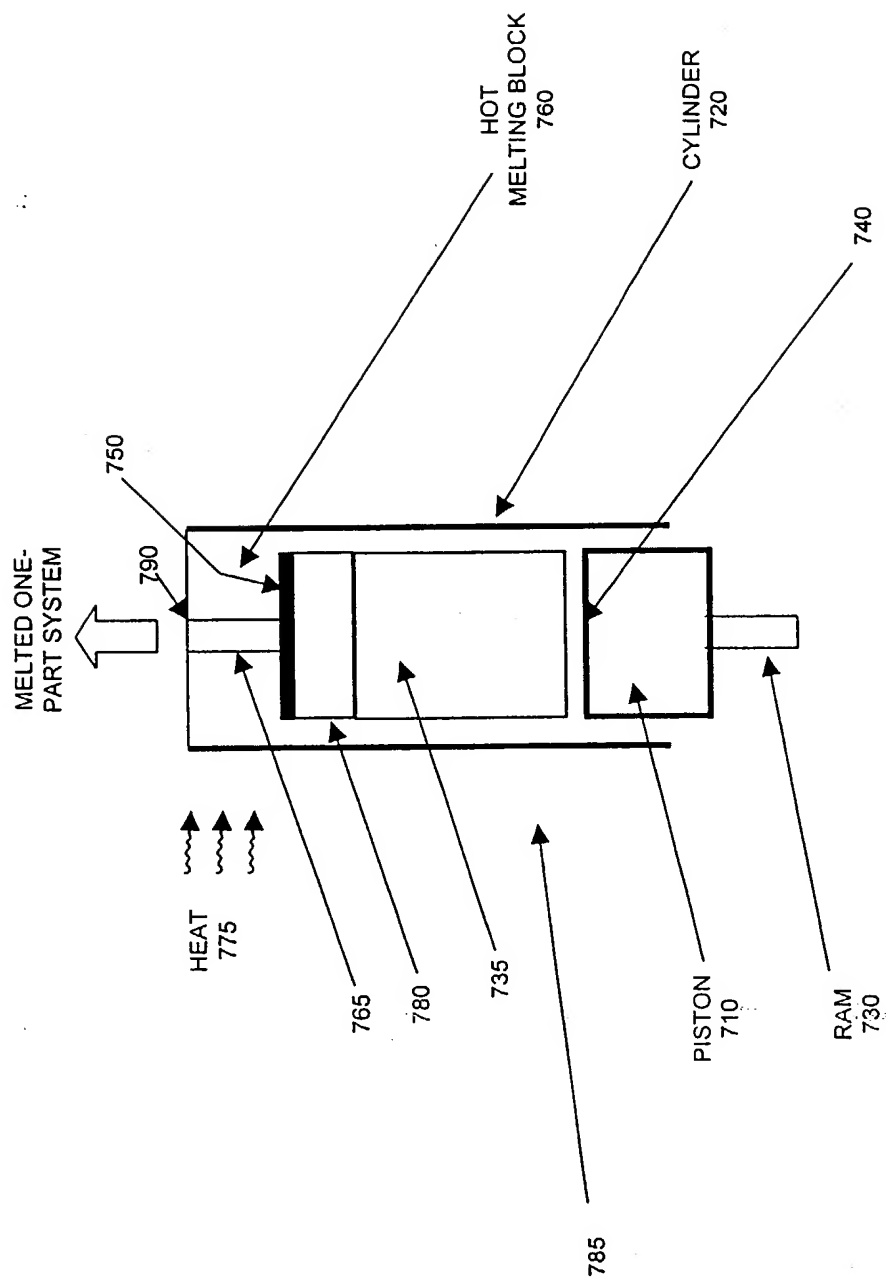


FIG. 7 PISTON TYPE MELTER FOR MELTING THE BLEND MATERIAL



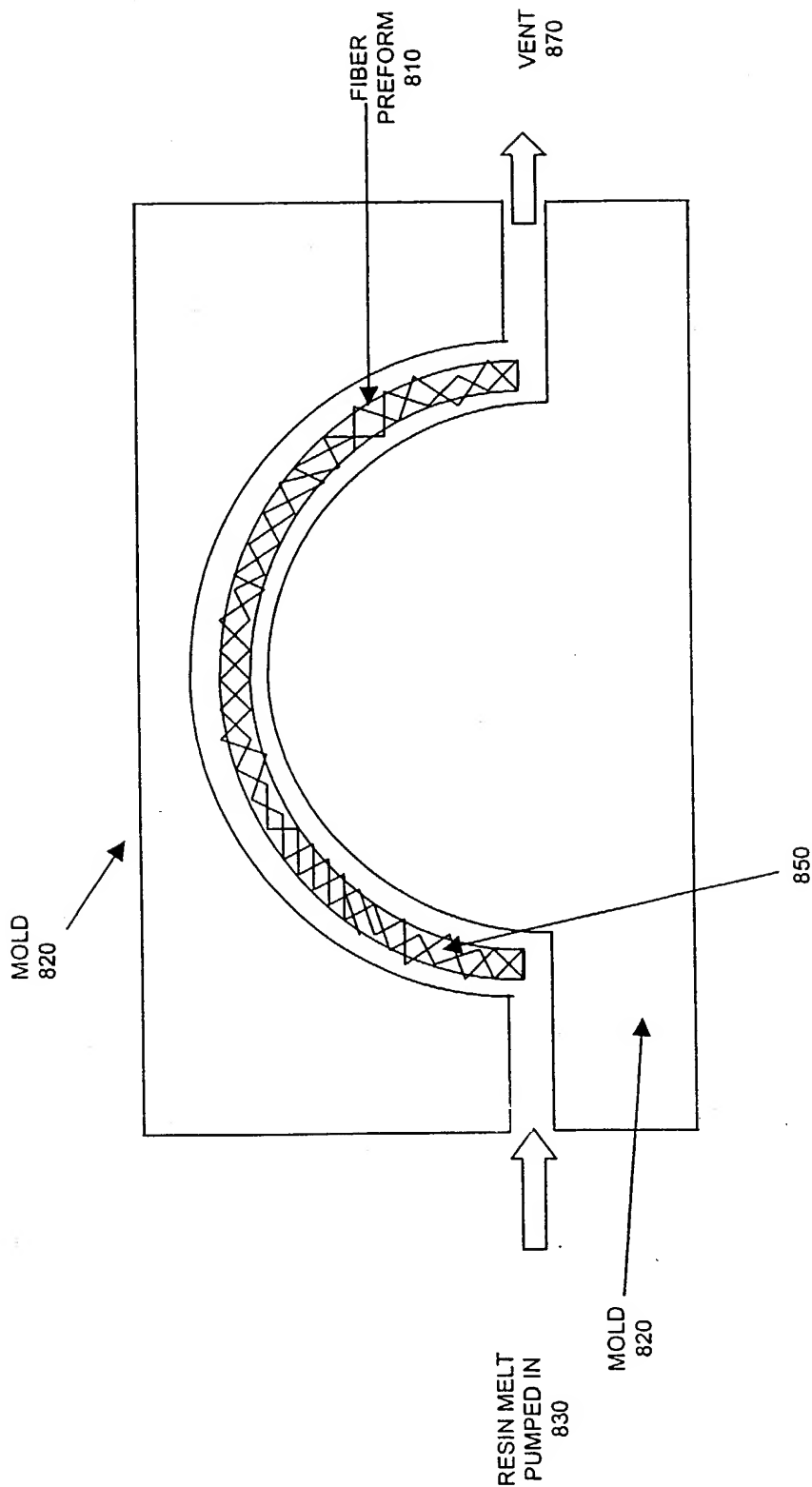


FIG. 8 RESIN TRANSFER MOLDING PROCESS

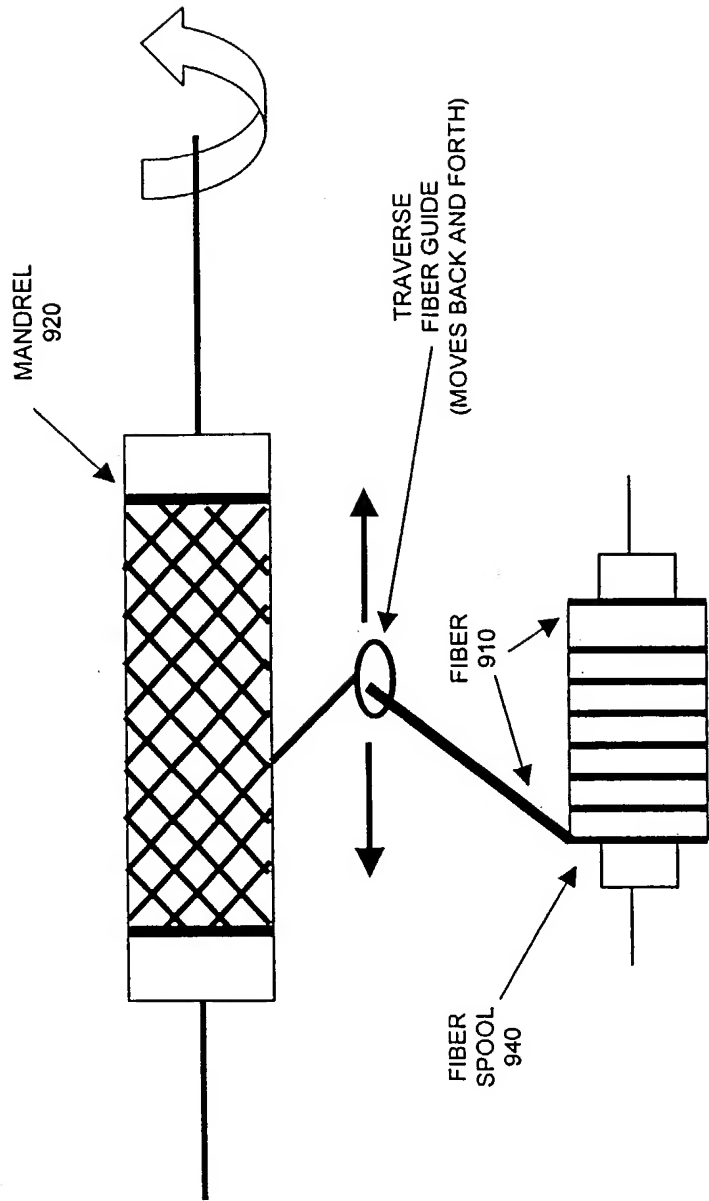
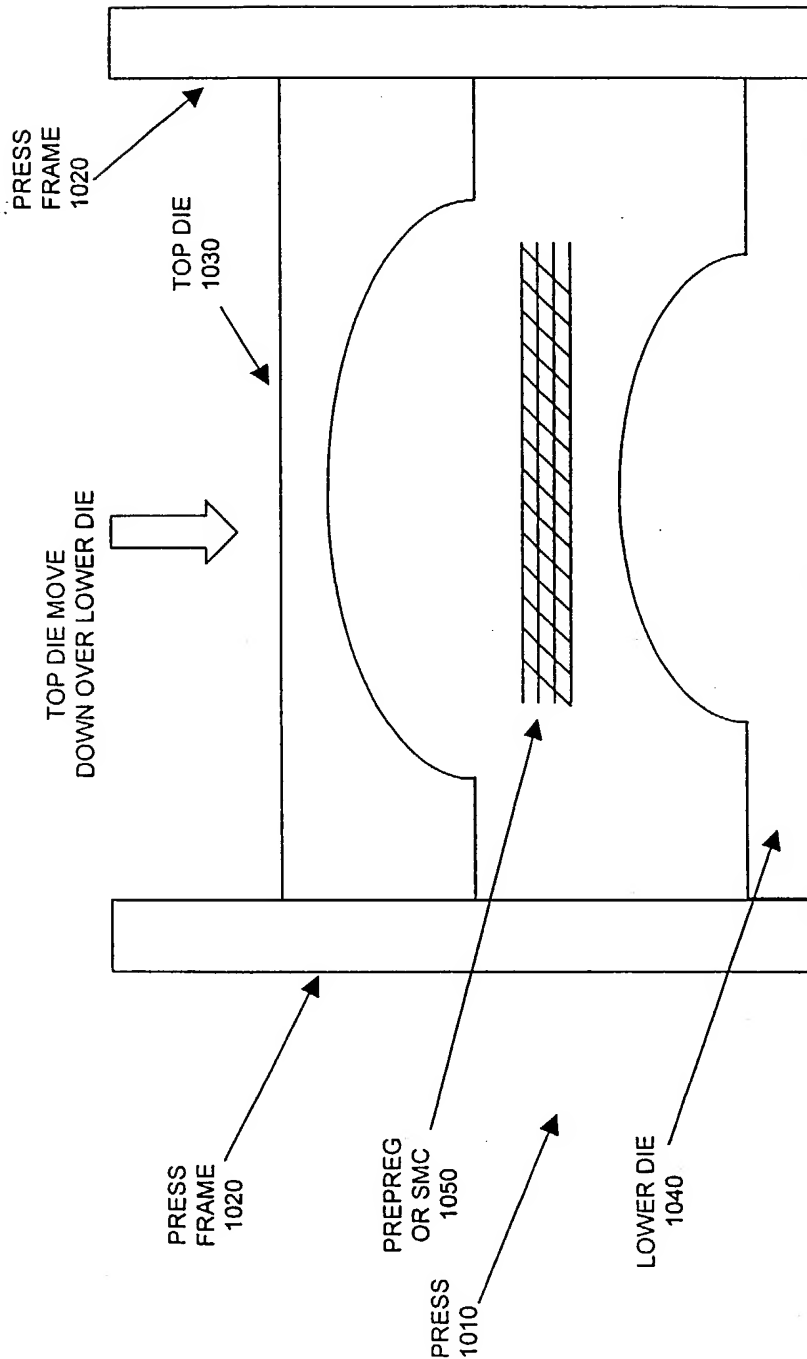
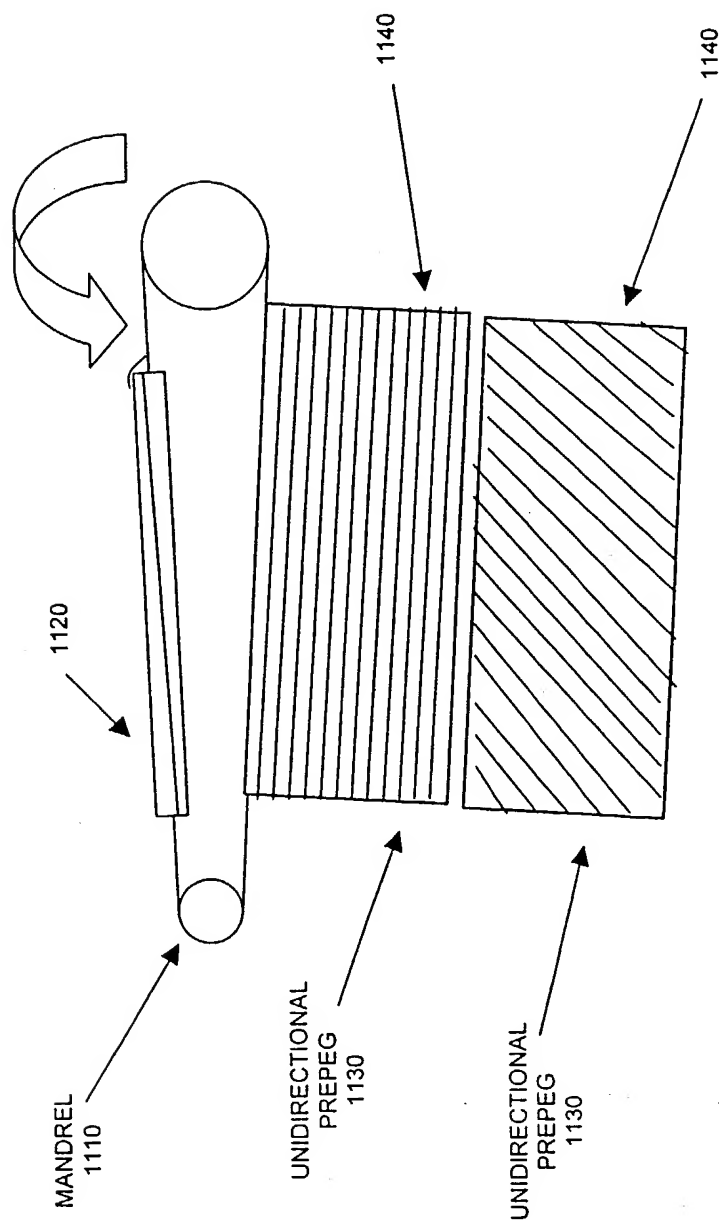


FIG. 9 FILAMENT WINDING PROCESS



**FIG. 10 COMPRESSION MOLDING PROCESS**



**FIG. 11 ROLL WRAPPING PROCESS**

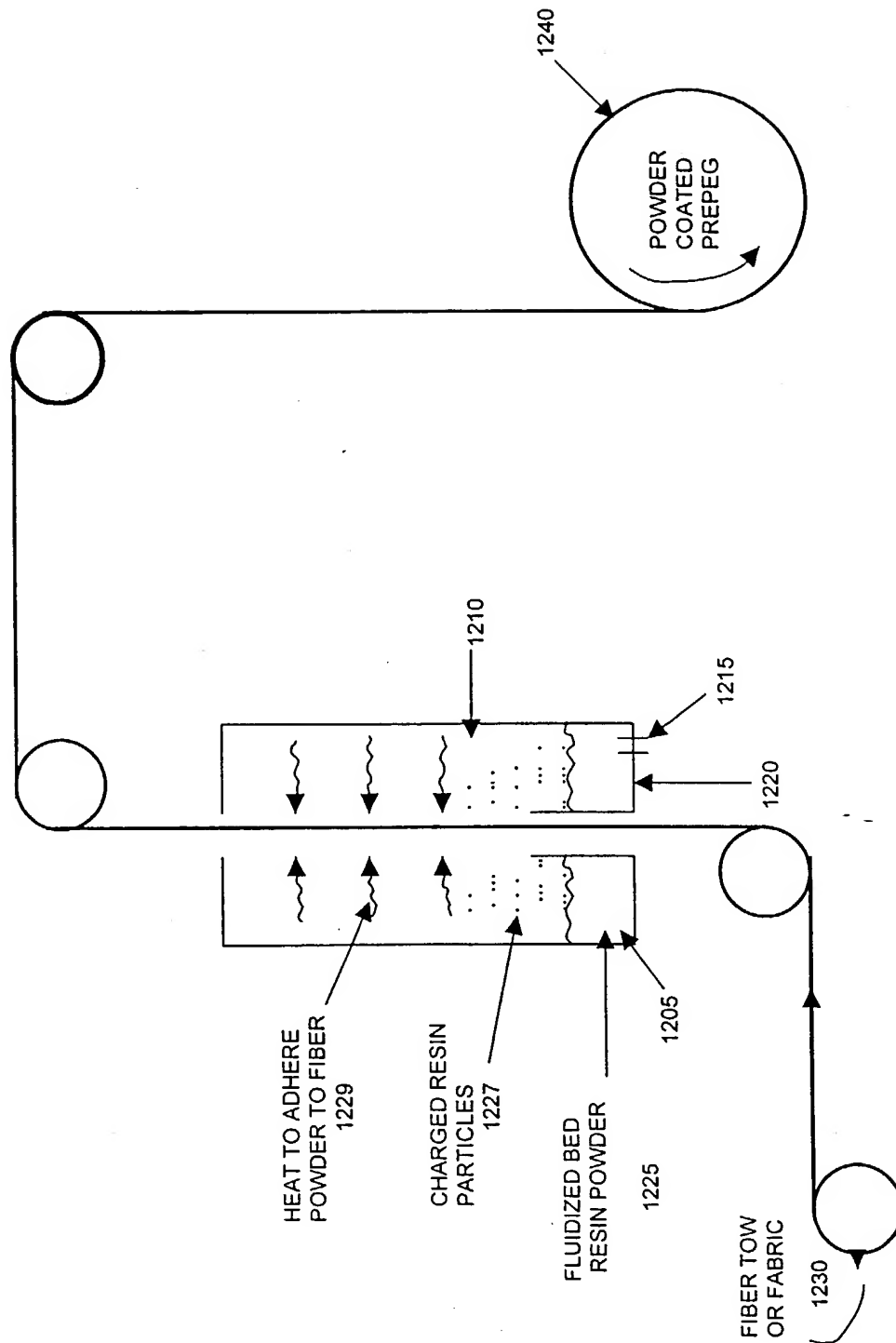


FIG. 12 POWDER COATING PROCESS

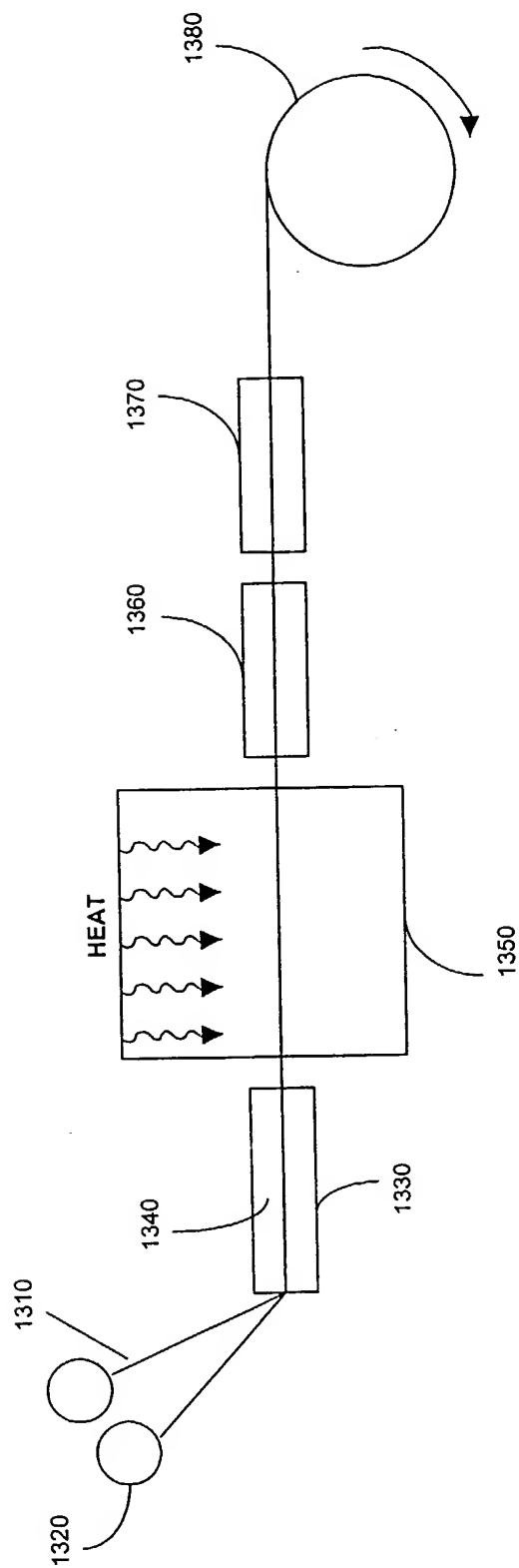
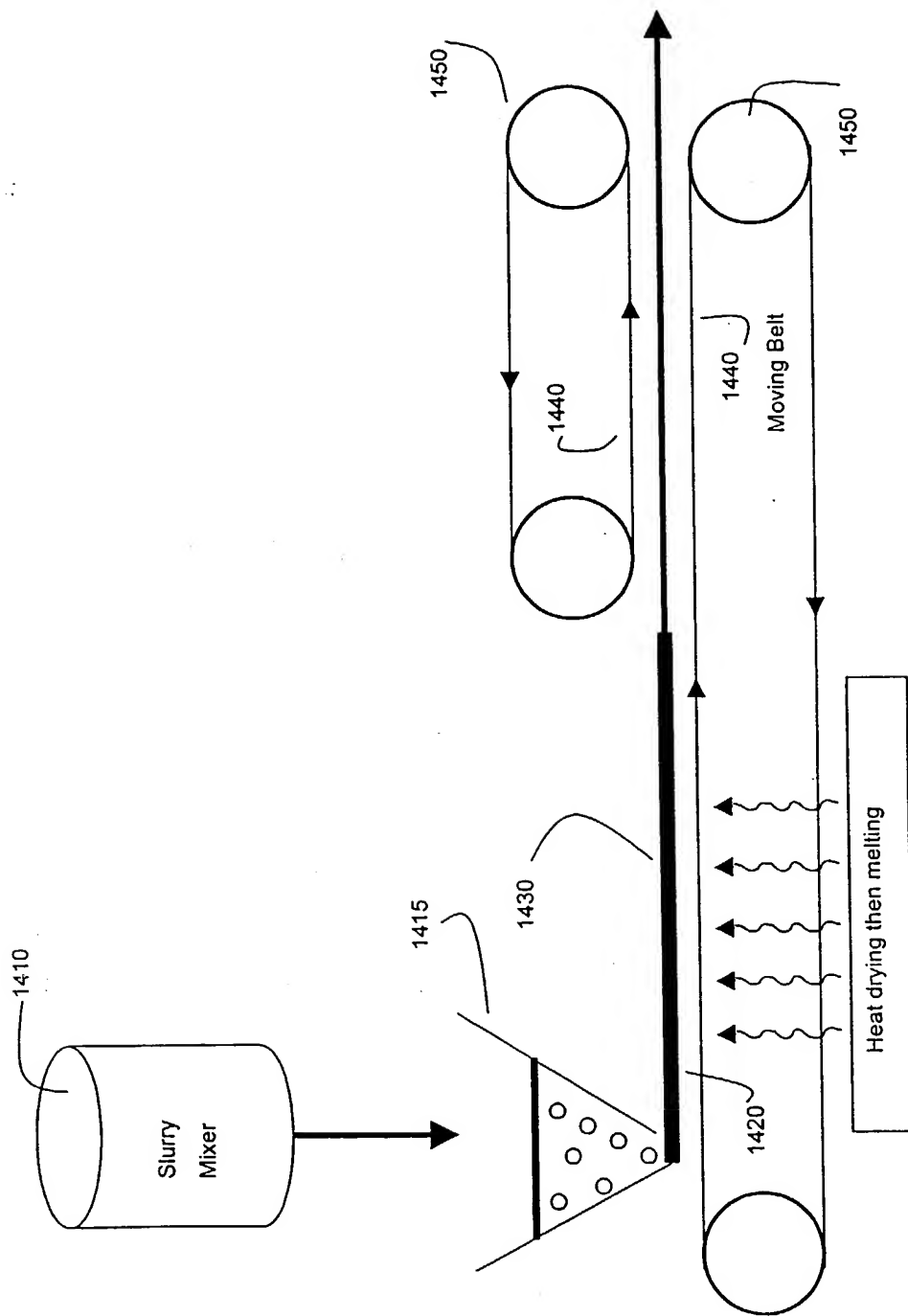


FIG. 13 WATER SLURRY PROCESS (A)



**FIG. 14 WATER SLURRY PROCESS (B)**



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BOSTON, MA 02110

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## Continuing Data as Claimed by Applicant

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11-6-00  
Date

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Date

## Title

SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND  
COMPOSITIONS PREPARED THEREBY

## Preliminary Class

528

Data entry by : SYDNOR, RUTH

Team : OIPE

Date: 11/02/2000





PATENT

Atty. Docket No.: CYC-037 (1591/14)

5 SPECIES MODIFICATION IN MACROCYCLIC  
POLYESTER OLIGOMERS, AND COMPOSITIONS  
PREPARED THEREBY

Technical Field

10 This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to macrocyclic polyester oligomer compositions and methods for modifying physical and chemical properties of the compositions. Even more particularly, this invention relates to macrocyclic polyester oligomer compositions having relatively low melting temperatures.

15 Background Information

Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss and solvent resistance. Linear polyesters are conventionally prepared by the  
20 reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding. Linear polyesters may be produced from macrocyclic polyester oligomers.

25 Macrocyclic polyester oligomers (MPOs) have unique properties that make them attractive as matrices for engineering thermoplastic composites. These desirable properties stem from the fact that MPOs exhibit low melt viscosity, allowing them to impregnate a dense fibrous preform easily. Furthermore, certain MPOs melt and polymerize at temperatures well below the melting point of the resulting polymer.  
30 Upon melting and in the presence of an appropriate catalyst, polymerization and crystallization can occur virtually isothermally. As a result, the time and expense required to thermally cycle a tool is favorably reduced.

Generally speaking, MPO compositions have high melting temperatures, which necessitate the use of special equipment in processing not commonly available in polymer processing units. If compositions with lower melting temperatures could be produced, it would be possible to use more readily available processing equipment  
5 such as that is commonly used in the production and handling of epoxy resins.

### Summary of the Invention

Physical and/or chemical properties of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the  
10 constituent MPOs. For example, the presence of a single MPO species, the macrocyclic polyester tetramer, has an unexpectedly pronounced effect on the melting temperature of a MPO composition. Removal of a portion of the macrocyclic polyester tetramer can result in low-melting MPO compositions. The resulting MPO compositions have the further advantage, under many circumstances, of a greatly  
15 reduced tendency to crystallize at ambient temperatures, making it possible to combine them with fillers such as carbon or glass fibers to produce preregs easily convertible to filled high molecular weight linear polyesters.

In one aspect, the invention is related to a process for modifying a physical property of a composition that includes MPOs. The process includes the steps of (a)  
20 providing a composition that has at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition.

In another aspect, the invention is related to a MPO composition that includes at least two species of MPOs wherein a species of the MPOs having the highest melting temperature is present in an amount less than or equal to 5%. In one  
25 embodiment, a blend material includes such a MPO composition and also a polymerization catalyst.

In a preferred embodiment, a MPO composition of the invention comprises 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers.

30 The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following figures, description, and claims.

### Brief Description of Figures

The drawings are not necessarily to scale, emphasis instead being generally placed upon illustrating the principles of the invention to facilitate its understanding.

5        FIG. 1 is a schematic illustration of an embodiment of the invention including a fractional crystallization process.

### Detailed Description

10        Physical properties, for example, the melting temperatures, of a composition comprising MPOs may be modified by modifying the weight percentage of a MPO species, for example, the macrocyclic polyester tetramer. A MPO composition having a low melting temperature can be polymerized and processed at lower temperature thereby avoiding the need for special equipment not commonly available in polymer processing.

### 15        Definitions

The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

As used herein, "macrocyclic" means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected  
20        to form the ring.

As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

As used herein, a "macrocyclic polyester oligomer (MPO)" means a macrocyclic oligomer containing structural repeat units having an ester functionality.  
25        A MPO typically refers to multiple molecules of one specific formula. However, a MPO also may include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. In addition, a MPO may be a macrocyclic co-polyester oligomer (including macrocyclic multi-polyester oligomer), i.e., an oligomer having two or more different structural repeat units having an ester  
30        functionality within one cyclic molecule.

As used herein, "degree of polymerization (DP)" means the number of identifiable structural repeat units in oligomeric or polymeric backbone. The structural repeat units may have the same or different molecular structural. For example, "macrocyclic polyester tetramer" or "tetramer" refers to MPOs with a DP of

5 4.

As used herein, a "species" means MPOs having the same DP. For example, the macrocyclic polyester tetramer is one species.

As used herein, a "macrocyclic polyester oligomer composition" means a composition comprising a mixture of MPOs having different DP values, whether or not units of more than one molecular structure are present.

As used herein, a "blend material" means a mixture of two or more components including at least one MPO and at least one polymerization catalyst. Preferably the blend material is uniformly mixed. A blend material may also include a filler as well as other components recognized by a skilled artisan.

15 As used herein, "substantially homo- or co-polyester oligomer" means a polyester oligomer wherein the structural repeat units are substantially identical or substantially two different structural repeat units, respectively.

As used herein, "an alkylene group" means  $-C_nH_{2n}-$ , where  $n \geq 2$ .

As used herein, "a cycloalkylene group" means a cyclic alkylene group, -  
20  $C_nH_{2n-x}-$ , where x represents the number of H's replaced by cyclization(s).

As used herein, "a mono- or polyoxyalkylene group" means  $[-(CH_2)_m-O-]_n-$   $(CH_2)_m-$ , wherein m is an integer greater than 1 and n is an integer greater than 0.

As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic  
25 group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure within.

As used herein, "a filler" means a material other than a MPO or a polymerization catalyst that may be included in the blend material. A filler often is  
30 included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester

polymer product, and/or to increase the strength of the polyester polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silica, carbon black, titanium dioxide, organo bromides in combination with antimonium oxides, calcium carbonate, chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers.

As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as, a fibrous or particulate material. Illustrative examples of particulate materials are chopped fibers, glass microspheres, and crushed stone.

As used herein, "an equilibrated mixture" means a mixture of MPOs in thermodynamic or kinetic equilibration.

As used herein, "fiber" means any material with elongated structure such as polymer or natural fibers. The material can be fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

As used herein, a "tow" or "strand" means a group of fibers together, or a bundle of fibers, which are usually wound onto spools and may or may not be twisted. These tows or strands can be woven or knitted to form fabrics.

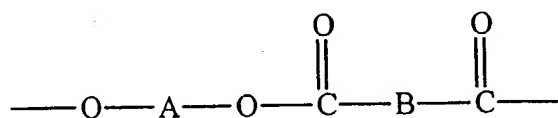
As used herein, a "fiber preform" means an assembly of fiber tows and/or fabric held together in a desired shape. Typically, fiber preforms are dry, and often held together with various tackifiers.

As used herein, a "prepreg" means a fiber material such as carbon fiber, glass fiber, or other fiber, that has been impregnated with a resin material in sufficient volume as to provide the matrix of the composite, and such that the ratio of fiber to resin is closely controlled. The fiber configuration can be in tow form, woven or knitted into a fabric, or in a unidirectional tape.

#### **I. Macrocyclic Polyester Oligomers (MPOs)**

Many different MPOs can readily be made and are useful in the practice of this invention. MPOs that may be employed in this invention include, but are not limited

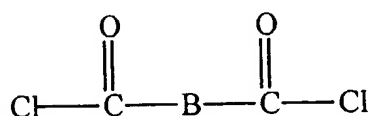
to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



5

where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group. MPOs that may be employed in this invention may have various DP values, e.g., 2 to 20, 2 to 10, 2 to 8, and 2 to 6.

MPOs may be prepared by known methods. Synthesis of the preferred MPOs may include the step of contacting at least one diol of the formula HO-A-OH with at least one diacid chloride of the formula:



15 where A and B are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such an amine is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is between about -25°C and about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

20 MPOs have also been prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate. The condensation typically occurs in the presence of a highly unhindered amine or a mixture thereof with at least one other tertiary amine such as triethylamine. Usually, a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof is used. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

25 Another method for preparing MPOs, including macrocyclic co-polyester oligomers, is to depolymerize linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to MPOs by heating a mixture of linear polyesters, an organic solvent, and a trans-

30

esterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

It is also within the scope of the invention to employ macrocyclic homo- and co-polyester oligomers to produce homo- and co-polyester polymers, respectively. Therefore, unless otherwise stated, an embodiment of a composition, article, or process that refers to a MPO may also include co-polyester embodiments.

Among homopolymeric compositions and in one embodiment, MPOs of poly(1,4-butylene) terephthalate (PBT) are used. Among homopolymeric compositions and in another embodiment, MPOs of polyethylene terephthalate (PET) are used. Among co-polymeric compositions and in one embodiment, MPO species contain a major proportion of PBT structural units, PET structural units, or both. In one embodiment, MPO species contain at least about 90 mole percent of PBT structural units, PET structural units, or both. In another embodiment, MPO species contain predominately PBT, and a minor proportion of other units, for example, poly(alkylene dicarboxylate) units or ether oxygen-containing units such as those in which A is derived from diethylene glycol.

## **II. Designing Physical and Chemical Properties of MPO Compositions**

In one embodiment, MPO compositions are created that have physical and/or chemical properties different from that of the unmodified MPO compositions originally produced. For example, the melting temperatures of a MPO composition can be significantly decreased by removal from the MPO composition of a major proportion of the macrocyclic polyester tetramer, i.e., the oligomer having a DP of 4. This is possible because the tetramer is both high melting and highly crystalline among the MPOs. Therefore, removal has a significant effect on the melting temperature and crystallinity of the oligomer composition. Similarly, the melting temperatures of a MPO composition can be significantly increased by adding into the MPO composition a significant proportion of the macrocyclic polyester tetramer.

In one aspect, the invention relates to a process for modifying a physical property of a composition having MPOs. The method includes the steps of (a) providing a composition having at least two species of MPOs, and (b) changing the

weight percentage of at least one species of the MPOs in the composition. It should be understood that compositions may have three, four, or five or more species of MPOs present. In addition, although preferably the weight percentage of one species of the MPOs in the composition is changed, the invention contemplates changing  
5 more than one species in a composition.

In one embodiment, the physical property to be modified is the melting temperature of the composition. Besides melting temperature, other physical properties that may be modified by the method of the invention include, for example, crystallinity and viscosity. Modification of a selected physical property may be  
10 achieved by either increasing or reducing the weight percentage of at least one species of the MPOs in the composition.

In one embodiment, the weight percentage of at least the species having the highest melting temperature is reduced in step (b). In one embodiment, the weight percentage of at least macrocyclic polyester tetramer is reduced in step (b). In one  
15 embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers. The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, a MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

20 The proportion of macrocyclic polyester tetramer present in products prepared by reactions under thermodynamic control is generally greater than the proportion resulting from reactions under kinetic control. An example of a thermodynamically controlled reaction is depolymerization. The reaction of a diol with a dicarboxylic acid chloride is chiefly kinetically controlled.

25 In one embodiment, the proportion of macrocyclic polyester tetramer removed according to the invention is at least 60% by weight of the total amount of the macrocyclic polyester tetramer in the oligomer composition as originally prepared. The amount of macrocyclic polyester tetramer present can vary according to the method of preparation of the oligomer composition. In another embodiment, at least  
30 70% of the macrocyclic polyester tetramer is removed. In yet another embodiment, at least 90% removal is performed.



In one embodiment, the reduction of the weight percentage of the macrocyclic polyester tetramer results in its weight percentage in the modified composition to be 60% less than its weight percentage in an equilibrated mixture of the MPOs according to the method of preparation. In another embodiment, the weight percentage  
5 reduction is 70%. In yet another embodiment, the weight percentage reduction is 90%.

Any processes that result in modification of the weight percentage of a species of the MPOs may be employed. The effectiveness of such processes may be dependent on factors including the nature of the original MPO composition and the  
10 particular species the proportion of which is to be modified. Illustrative examples of such processes include distillation, fractional crystallization, anti-solvent precipitation, addition and mixing, chemical reactions, etc.

In one embodiment, removal of a species of MPOs is achieved by fractional crystallization. In one embodiment, the macrocyclic polyester tetramer is removed by  
15 fractional crystallization from a solution of the MPO composition. Any solvent that facilitates fractional crystallization may be employed. Illustrative suitable solvents include aromatic hydrocarbons and halogenated aromatic hydrocarbons, such as toluene, xylene and *o*-dichlorobenzene (ODCB). For example, in one embodiment, a 5% by weight solution of oligomer composition in ODCB at 110°C is cooled to  
20 ambient temperature of about 25°C, whereupon a precipitate forms that contains a major proportion of the tetramer.

In one embodiment, removal of the macrocyclic polyester tetramer is achieved by anti-solvent precipitation. Illustrative suitable non-solvents include aliphatic hydrocarbons, especially those in the C<sub>6-10</sub> range such as hexane, heptane, octane and  
25 decane. In one preferred embodiment, heptane is used.

In one embodiment of a process of removing macrocyclic polyester tetramer by anti-solvent precipitation, the non-solvent is added to the MPO solution at an elevated temperature, in the range of about 80-120°C, after which the mixture is allowed to cool to a lower temperature, typically no higher than about 70°C since at  
30 lower temperatures substantial amounts of other oligomers, or the MPO composition in its entirety, may be precipitated. The amount of non-solvent added is most often about 90-110% by volume of solvent used. Upon cooling to this lower temperature, a

precipitate forms that is predominantly the macrocyclic polyester tetramer. A minor proportion of the macrocyclic polyester tetramer originally present usually remains in the MPO composition in solution. However, the remaining macrocyclic polyester tetramer does not have a significant effect on the melting temperature and crystallinity of the MPO composition.

The MPO species removed may be reused for various purposes. In one embodiment, the MPO species, e.g., macrocyclic polyester tetramer, is polymerized separately or in combination with other MPOs or linears to produce linear polyester. In another embodiment, the MPO species is equilibrated with linear polyester that is intended to be depolymerized, either before or during the depolymerization reaction. Depolymerization of a mixture of linear polyester and the MPO species removed from a MPO composition provides an oligomeric product that has the same distribution of oligomers as that obtained from linear polyester alone, showing that equilibration is essentially complete.

The apparatus for performing the above modification processes may be any conventional apparatus. The actual apparatus will depend on the actual process being employed. In one embodiment for performing fractional crystallization (referring to FIG. 1), an apparatus for producing the compositions of the invention may include a reactor vessel 110 in which the reaction constituents 120, e.g., linear polyester, solvent and depolymerization catalyst, are combined and the depolymerization reaction conducted. Subsequently, the product mixture passes through a filter 130 to remove linears. The filtrate may pass into a second vessel 140 where it is cooled to room temperature either in the presence or absence of aliphatic hydrocarbon as non-solvent to precipitate a species of MPO, e.g., the tetrameric species. The filtrate is then passed through another filter 150 which removes the precipitate, e.g., macrocyclic polyester tetramer. The precipitated macrocyclic polyester oligomers can be removed from the filter 150 and recycled to the reactor vessel 110. Further vessels may be employed downstream to isolate the product in the desired form and to remove non-solvent when it is employed.

In a preferred embodiment of the invention, a MPO composition includes at least two species of MPOs wherein the species having the highest melting temperature

is present in an amount less than or equal to 10%, preferably less than or equal to 5%, more preferably less than or equal to 3%.

In one embodiment, the MPOs in the MPO composition have a DP from 2 to about 20. In another embodiment, the MPOs have a DP from 2 to about 10. In  
5 another embodiment, the MPOs have a DP from 2 to about 8. In yet another embodiment, the MPOs have a DP from 2 to about 6.

In one embodiment, the species having the highest melting temperature is macrocyclic polyester tetramer. In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes  
10 macrocyclic PET oligomers. The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, the MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

In one embodiment, the MPO composition includes 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester  
15 tetramers, and 5-20% macrocyclic polyester pentamers. In some embodiments, the percentage of macrocyclic polyester tetramers preferably is less than about 3%, more preferably less than about 2%, or most preferably less than about 1%.

In one embodiment, the MPO composition includes a filler. In another embodiment, the MPO composition includes a polymerization catalyst. In another  
20 embodiment, the MPO composition is part of a prepreg composition.

MPO compositions in which a major proportion of the macrocyclic polyester tetramer has been removed have melting temperatures significantly lower than those of corresponding compositions containing macrocyclic polyester tetramer in the original proportions, i.e., the unmodified product mixtures (equilibrated or nearly  
25 equilibrated) of the MPO-forming reactions. The melting temperatures typically are wide ranges by reason of the various kinds of MPO molecules in the MPO compositions. The most pronounced decrease in temperature is in the upper value of the range, i.e., the temperature at which the last trace of solid melts. Typically, the upper value of the melting temperature range of a modified MPO composition may be  
30 from about 15°C to as much as 70°C lower than the upper value for the unmodified original MPO composition.

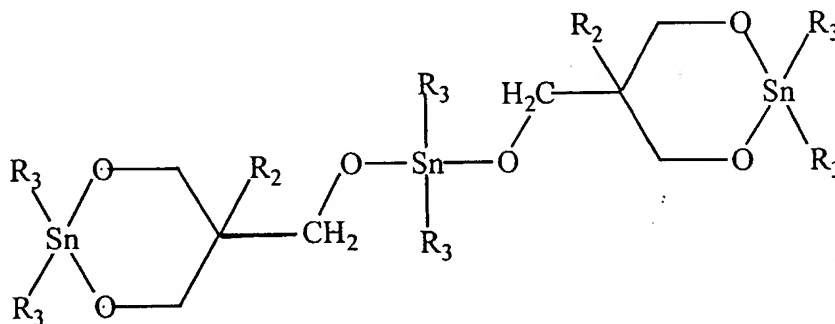
This decrease in melting temperature is typically accompanied by a significant decrease in crystallinity, particularly upon heating above the melting temperature followed by quenching. Thus, MPO compositions in which macrocyclic polyester tetramer has been removed can be quenched and used to impregnate fibrous or other fillers, whereupon a prepreg composition capable of being draped and shaped is produced.

### III. Polymerization catalysts

Polymerization catalysts that may be employed in the invention are capable of catalyzing the polymerization of MPOs. Organotin and organotitanate compounds are preferred catalysts, although other catalysts may be used. For example, organotin compound 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane may be used as polymerization catalyst. Other illustrative organotin compounds include n-butyltin(IV) chloride dihydroxide, dialkyltin(IV) oxides, such as di-n-butyltin(IV) oxide and di-n-octyltin oxide, and acyclic and cyclic monoalkyltin (IV) derivatives such as n-butyltin tri-n-butoxide, dialkyltin(IV) dialkoxides such as di-n-butyltin(IV) di-n-butoxide and 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and trialkyltin alkoxides such as tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.*

Also, trisstannoxanes having the general formula (I) shown below can be used as a polymerization catalyst to produce branched polyester polymers.

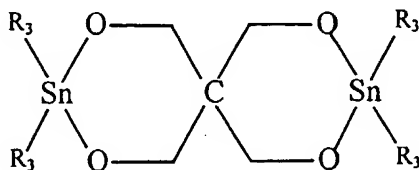
(I)



where  $R_2$  is a  $C_{1-4}$  primary alkyl group and  $R_3$  is  $C_{1-10}$  alkyl group.

Additionally, organotin compounds with the general formula (II) shown below can be used as a polymerization catalyst to prepare branched polyester polymers from MPOs.

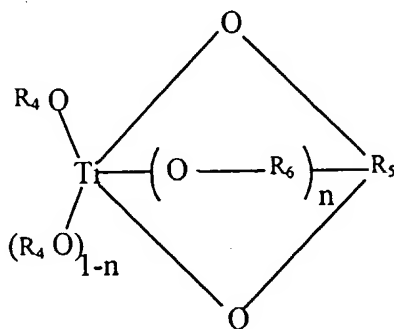
(II)



5 where R<sub>3</sub> is defined as above.

As for titanate compounds, tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds with the general formula (III) shown below can be used as polymerization catalysts.

(III)

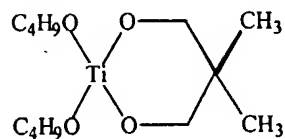


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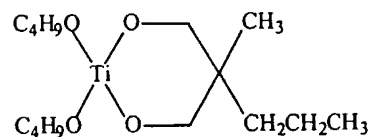
wherein: each R<sub>4</sub> is independently an alkyl group, or the two R<sub>4</sub> groups taken together form a divalent aliphatic hydrocarbon group; R<sub>5</sub> is a C<sub>2-10</sub> divalent or trivalent aliphatic hydrocarbon group; R<sub>6</sub> is a methylene or ethylene group; and n is 0 or 1.

15 Typical examples of titanate compounds with the above general formula are shown in Table 1.

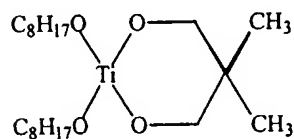
**Table 1.** Examples of Titanate Compounds Having Formula (III)



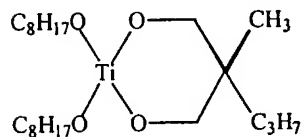
Di-1-butyl 2,2-dimethylpropane-1,3-dioxytitanate



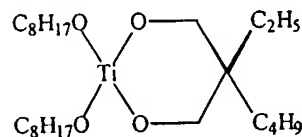
Di-1-butyl 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate



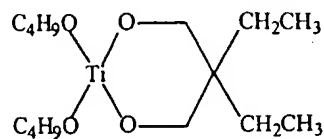
Di(2-ethyl-1-hexyl) 2,2-dimethylpropane-1,3-dioxytitanate



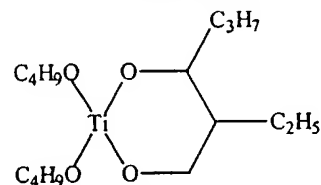
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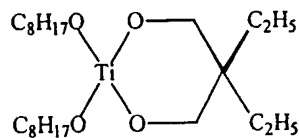
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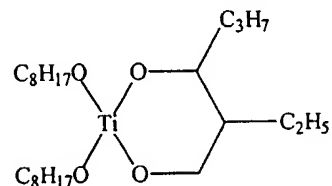
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Di-1-butyl 2-ethylhexane-1,3-dioxytitanate

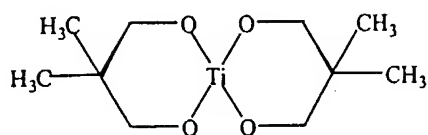


Di(2-ethyl-1-hexyl) 2,2-diethylpropane-1,3-dioxytitanate

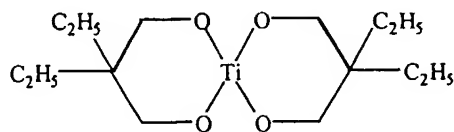


Di(2-ethyl-1-hexyl) 2-ethylhexane-1,3-dioxytitanate

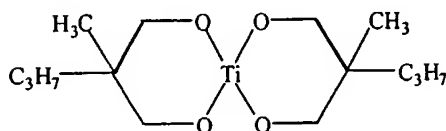
**Table 1.** Examples of Titanate Compounds Having Formula (III) (Cont'd)



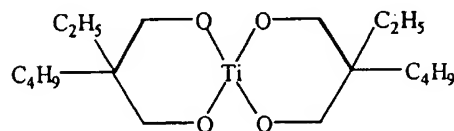
Bis(2,2-dimethyl-1,3-propylene) titanate



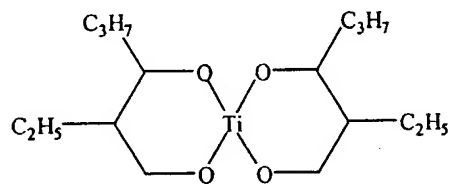
Bis(2,2-diethyl-1,3-propylene) titanate



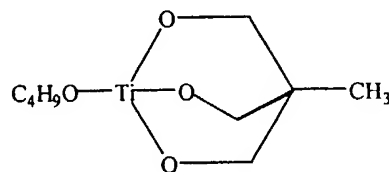
Bis(2-(1-propyl)-2-methyl-1,3-propylene) titanate



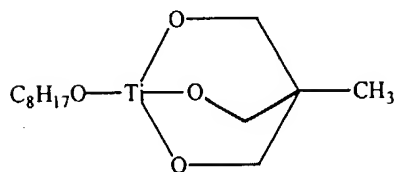
Bis(2-(1-butyl)-2-ethyl-1,3-propylene) titanate



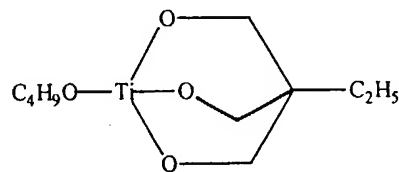
Bis(2-ethyl-1,3-hexylene) titanate



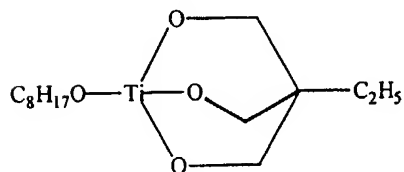
1-(1-Butoxy)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane-1-titanabicyclo[2,2,2]octane



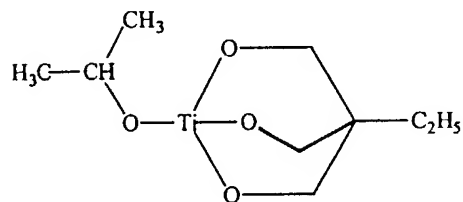
1-(2-ethyl-1-hexoxy)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane-1-titanabicyclo[2,2,2]octane



1-(1-Butoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane-1-titanabicyclo[2,2,2]octane



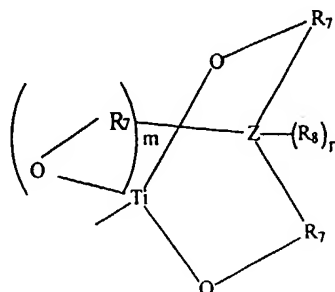
1-(2-ethyl-1-hexoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane-1-titanabicyclo[2,2,2]octane



1-(2-Propoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane-1-titanabicyclo[2,2,2]octane

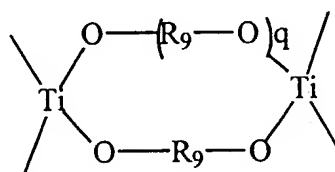
Titanate ester compounds having at least one moiety of the following general formula have also been used as polymerization catalysts:

(IV)



5 or

(V)



wherein:

each  $R_7$  is independently a  $C_{2-3}$  alkylene group;

10  $R_8$  is a  $C_{1-6}$  alkyl group or unsubstituted or substituted phenyl group;

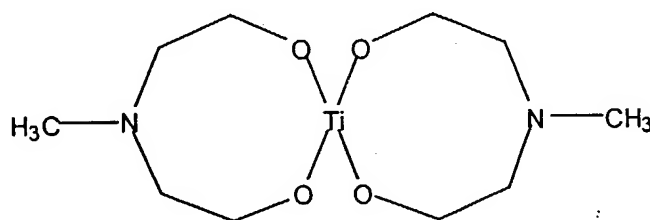
$Z$  is O or N; provided when  $Z$  is O,  $m = n = 0$ , and when  $Z$  is N,  $m = 0$  or 1 and  $m + n = 1$ ;

each  $R_9$  is independently a  $C_{2-6}$  alkylene group; and  $q$  is 0 or 1.

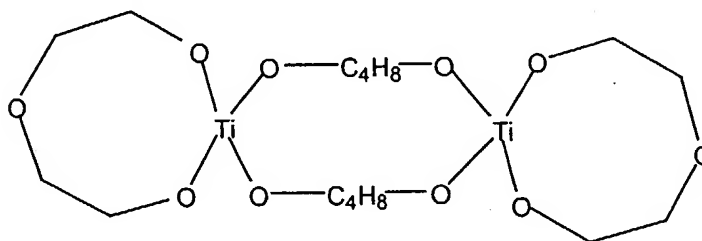
Typical examples of such titanate compounds are shown below as formula

15 (VI) and formula (VII):

(VI)



(VII)





#### IV. The Blend Material

A blend material comprising MPOs and a polymerization catalyst allows for easy production, storage, transportation and processing. From the standpoint of applications, the blend material is a one-component ready-to-use mixture. The blend material may also be processed like a thermoset while producing a thermoplastic. Furthermore, the blend material may eliminate the need for existing equipment to be modified to allow for transfer of the MPO and a polymerization catalyst into the equipment in the appropriate amounts at the appropriate time and at the appropriate temperature.

10 In one aspect, the invention relates to a blend material comprising a MPO composition with a modified physical property (e.g., the melting temperature as described above) and a polymerization catalyst.

There is no limitation with respect to the physical form of the MPO when mixed with the polymerization catalyst as long as the MPO remains substantially chemically intact. In one embodiment, the MPO is a solid such as a powder. In this embodiment, mechanical mixing typically is used to mix MPO with a polymerization catalyst. In another embodiment, the MPO is mixed in the presence of a solvent with the solvent remaining present during the step of mixing.

15 In one embodiment, the blend material also includes a filler as described above. Illustrative examples of such fillers include pigments, light weight fillers, flame retardants, and ultraviolet light stabilizers. For example, calcium carbonate may be used to increase the thickness of a polyester polymer product to improve its mechanical performance. Also, glass microspheres may be added to lower the density of the product. Other fillers include nanoclays, e.g., to increase the modulus of the product, organo bromides in combination with antimony oxides, e.g., to impart flame resistance, and colorants such as carbon black or titanium dioxide.

20 The filler is added generally between about 0.1% and 70% by weight, between about 25% and 70% by weight, or between about 2% and 5% by weight depending on the filler and the purpose for adding the filler. For example, the percentage is preferably between 25% and 50% by weight in the case of calcium carbonate, between 2% and 5% by weight in the case of nanoclays, between 0.1% and 1% in the case of pigments, and between 25% and 70% by weight in the case of glass microspheres.

A process for preparing the blend material includes providing a MPO and mixing the MPO with a polymerization catalyst. When preparing the blend, the MPO and the polymerization catalyst may be mixed together by various means. For example, any conventional mixer or blender may be employed to mix the MPO with  
5 the polymerization catalyst via agitation at temperatures below the melting temperature of the MPO. This process may be conducted under an inert atmosphere such as a nitrogen atmosphere.

A solvent may also be employed to assist in the uniform mixing of the MPO with the polymerization catalyst. Various solvents can be used, and there is no  
10 limitation with respect to the type of solvent that may be used other than that the solvent is substantially free of water. Illustrative examples of solvents that may be employed in the invention include methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, benzene, toluene, *o*-xylene, chlorobenzene, dichloromethane, and chloroform.

15 There is no limitation with respect to the amount of solvent to be employed other than that the amount results in a uniform mixing of the MPO and the polymerization catalyst. In one embodiment, the blend of MPO with the polymerization catalyst is isolated either by direct removal of the solvent via evaporation or by precipitation via addition of the mixture into a nonsolvent. In  
20 another embodiment, the blend of solid ingredients is further dried under vacuum at elevated temperatures below the melting temperature of the MPO to remove any residual solvent.

A process for preparing the blend material further having at least one filler, or any other additional material, is generally the same as described above, however, the  
25 characteristics of the filler and/or additional materials must be considered. It should be understood that the MPO, the polymerization catalyst, the filler, any additional material(s) and/or solvent, if used, may be mixed in any order or simultaneously as long as the final composition contains the appropriate amount of each ingredient.

It is within the scope of the invention to employ one, two or more different  
30 fillers in preparing a blend material of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to filler in singular also includes an embodiment wherein two or more different

fillers are employed. Similarly, unless stated otherwise, any embodiment of a composition, article or process that refers to fillers in plural also includes an embodiment wherein one filler is employed.

5 In one embodiment of the invention, the amount of polymerization catalyst employed is generally about 0.01 to about 10.0 mole percent, preferably about 0.1 to about 2 mole percent, and more preferably about 0.2 to about 0.6 mole percent based on total moles of monomer repeat units of the MPO.

Although dependent on the particular composition of the blend material, blend materials typically exhibit a shelf life generally longer than a week, and preferably  
10 longer than a month, and more preferably longer than a year when stored at ambient temperature.

It is within the scope of the invention to employ one, two or more different polymerization catalysts in preparing a blend of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or  
15 process that refers to polymerization catalyst in singular also includes an embodiment wherein two or more different polymerization catalysts are employed. Similarly, unless stated otherwise, any embodiment of a composition, article or process that refers to polymerization catalyst in plural also includes an embodiment wherein one polymerization catalyst is employed. Two or more polymerization catalysts may be  
20 used to vary the rate of polymerization and to produce polyesters with variable degrees of branching.

#### V. Polymerization of MPOs

In another aspect, the invention relates to a process for polymerizing a MPO  
25 composition that includes the steps of (a) providing a MPO composition with a modified physical property (e.g., the melting temperature as described above), (b) providing a polymerization catalyst, and (c) polymerizing the MPOs. The MPOs and the polymerization catalyst may be components of a blend material. Therefore, in one embodiment, a process for polymerizing a MPO composition includes the steps of (a)  
30 providing a blend material having a MPO composition with a modified physical property, e.g., the melting temperature, and (b) polymerizing the MPOs. In one embodiment, the polymerization is conducted in the range of 130 °C to 230 °C.

By reason of the lower melting temperature and decrease in crystallinity, it is frequently possible to polymerize the compositions of the present invention to linear polyesters at lower temperatures than with previously known MPO compositions. For example, a conventionally prepared macrocyclic PBT oligomer composition may  
5 require a polymerization temperature (in the presence of a conventional tin compound as catalyst) on the order of 190°C and will not polymerize at 150°C. The corresponding composition, from which most of the tetramer has been removed according to this invention, has been polymerized to high molecular weight PBT at temperatures as low as 148°C.

10 In other respects, the compositions of MPOs in which tetramers have been removed are similar to known MPO compositions in that they may be polymerized under a wide variety of conditions in the presence of polymerization catalysts to linear polyesters having a wide variety of uses.

Blends of MPOs with catalyst and/or filler may be polymerized in processes  
15 such as rotational molding, resin film infusion, pultrusion, resin transfer molding, filament winding, making and using powder-coated or hot melt prepreg, water slurry process, compression molding, and roll wrapping. These processes may be used to form polyester compositions, including composites, which may be included in articles of manufacture such as carbon fiber golf shafts and lightweight automotive chassis  
20 members, construction materials, and so on.

The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention.

#### ***Example A General Depolymerization Procedure***

25 Dissolve dry poly(1,4-butylene terephthalate) (PBT) pellets in dry *o*-dichlorobenzene (ODCB) under inert atmosphere at 180°C. Add a titanate catalyst as a solution in ODCB or as a neat solid. The depolymerization reaction is carried out at about 180°C. The reaction can be sampled over time to determine progress. When equilibrium is reached (usually within 1 hour), the reaction is cooled to 100°C and  
30 water is added to quench the titanate catalyst (add about 0.5% water by volume).

After quenching, the reaction mixture is concentrated by removing 70-95% of the ODCB. This step can be done from 70-180°C by adjusting pressure during the strip.

After the initial concentration step, the reaction is allowed to cool to about 70°C and filtered to remove the bulk of the linears which fall from solution. The filtrate, which contains the MPOs, is concentrated to about 30% solids at about 110°C. An equal volume of heptane is added and the reaction is allowed to cool to about 70°C to precipitate the PBT tetramer. Filter to remove the PBT tetramer and pass the filtrate through a column of alumina to remove residual linears. Pure MPOs are then isolated by heptane precipitation or by concentration.

PBT used in these experiments was produced by General Electric (Valox 315 grade) and was dried in *vacuo* at about 120°C before use. Anhydrous ODCB was used as received from Aldrich. Titanate catalysts were prepared from tetraisopropyl titanate from DuPont that was vacuum distilled prior to use. Diols that were dried over molecular sieves. All other reagent grade solvents and chemicals were used as received.

HPLC analysis was used to characterize the composition of the MPOs and to follow progression of depolymerization reactions. HPLC analysis was conducted using a Hewlett Packard Series 1050 chromatography system. Samples were eluted at 1.5 ml/min through a 4.6 x 15 cm Zorbax Eclipse XBD-C8 column at 40°C. A linear acetonitrile:water gradient which ramped from 50:05 to 100:0 over 18 min was used. Analysis was calibrated using pure PBT dimer which was isolated by vacuum sublimation. MPOs were quantified using phenanthrene as an internal calibration standard. Peaks were measured at 254 nm with a UV detector.

Analyses for polymer  $M_w$  were conducted using a Hewlett Packard Series 1100 chromatography system. Samples were eluted at 1 ml/min with chloroform through a bank of two Phenomenex Phenogel 5 $\mu$ m linear 300 x 7.8 mm columns at 40°C. Peaks were detected with a UV detector at 254 nm and the instrument was calibrated using polystyrene standards.

HPLC retention times of MPOs are shown in Table 1. Melting range data of select MPO compositions is shown in Table 2.

**Table 1. HPLC Retention Times of Select MPOs**

MPO	Dimer (PBT)	Trimer (PBT)	Tetramer (PBT)	Pentamer (PBT)
HPLC T <sub>r</sub> (min.)	6.8	11.5	13.6	15.4

**Table 2. Melting Ranges of Select MPO Compositions**

Sample	%Dimer	%Trimer	%Tetramer	%Pentamer	% co-MPO	Melt Range °C
a	13.1	12.9	51.9	11.7	9.3	175-218
b	2	46.7	29.8	21.5	0	120-215
c	32.2	38.2	16.6	13.1	0	120-200
d	34.5	29.9	12.8	11.2	13.8	125-175
e	30.6	34.3	10.2	10.2	14.2	125-168
f	37.1	37	1.48	10	14.5	125-148

**5 Example 1**

A 22.2 g sample of commercially available PBT was dissolved in 1,450 g (1,107 ml) of ODCB and depolymerized in the presence of 2.8 mole percent of a mixed 1,4-butanediol/2-methyl-2,4-pentanediol (4.3:1 molar) titanate catalyst. MPOs were obtained in the amount of 11.4 g, or 51.8% of theoretical.

10 The reaction mixture was quenched with water at 100°C and ODCB was distilled off to a MPO concentration of 11% by weight (71 ml of ODCB). A sample was removed and stripped of solvent; it was found to have a melting temperature of 100-210°C.

Heptane, 71 ml, was added to the remaining oligomer composition at 110°C  
 15 and the reaction mixture was allowed to cool to 70°C, whereupon a precipitate formed. The mixture was filtered; the filtration residue was found by HPLC analysis to contain about 96% by weight of the tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-150°C.

20

**Example 2**

A 250 ml round-bottomed flask equipped with a magnetic stirrer was charged with 85 g (64 ml) of ODCB and 15 g of a macrocyclic PBT oligomer composition prepared by the reaction of terephthaloyl chloride with bis(4-hydroxybutyl)

terephthalate. A control sample of the oligomer composition was found to have a melting temperature of 100-180°C.

Heptane, 64 ml, was added slowly to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool over 1 hour to 75°C, whereupon a precipitate formed. The mixture was filtered; the filtration residue was found to contain about 90% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-130°C.

#### 10 *Example 3*

A 3 l round-bottomed flask equipped with a magnetic stirrer and thermometer was charged with 700 g (534 ml) of ODCB and 300 g of a macrocyclic PBT oligomer composition prepared by the reaction of terephthaloyl chloride with 1,4-butanediol. A control sample of the oligomer composition was found to have a melting temperature of 120-175°C.

The mixture was heated to 110°C to dissolve all of the oligomers and heptane, 534 ml, was added slowly at 110°C. The reaction mixture was allowed to cool to 75°C, whereupon a precipitate formed. The mixture was filtered; the filtration residue was found to contain about 73% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 120-158°C.

#### *Example 4*

A 5% (by weight) solution in ODCB of macrocyclic PBT oligomers, prepared as described in Example 1, was found to be a homogeneous liquid at 110°C. Upon cooling to room temperature, a precipitate deposited from the solution. The precipitate was found by analysis to be 90% pure cyclic tetramer, and to constitute 60% by weight of the tetramer present in the original oligomer composition.

#### 30 *Example 5*

A 300 mg control sample of the PBT oligomer composition employed in Example 2, from which the tetramer had not been removed, was placed in a test tube and submerged in an oil bath maintained at 150°C for 10 minutes. The composition did not melt at this temperature. A sample of the product of Example 2, from which  
5 tetramer had been removed, melted when heated to the same temperature but crystallized to an opaque, brittle solid upon cooling.

When the product of Example 2 was heated to 150°C and quenched by submersion in cold water, it remained transparent, indicating that it was amorphous rather than crystalline after quenching. It remained amorphous and tacky after storing  
10 at ambient temperature for one month. By contrast, the control returned to a brittle, crystalline state upon standing for 48 hours.

#### ***Example 6***

A 3 l round-bottomed flask was charged with 3,098 ml of ODCB, 26.3 g of  
15 commercially available PBT pellets, and 4.9 g of tetramer removed from a MPO composition as described in Example 3. The resulting mixture was heated to 180°C until all solids were dissolved and a titanate catalyst similar to that of Example 1 was added in a similar proportion to PBT. Heating at 180°C was continued for one hour, after which a portion of the mixture was analyzed and found to contain MPOs in a  
20 proportion similar to that observed in Example 1.

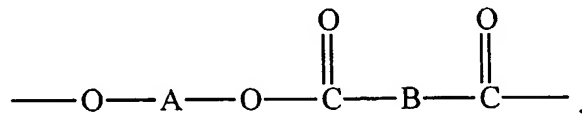
While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions and examples should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and  
25 scope of the present invention.

The patents and references referred to above are incorporated by reference including: U.S. Patent Nos. 5,039,783, 5,191,013, 5,231,161, 5,348,985, 5,389,719, 5,407,984, 5,466,744, 5,591,800, 5,661,214, 5,668,186, and 5,710,086.

30 What is claimed is:



- 1 1. A process for modifying a physical property of a composition comprising  
2 macrocyclic polyester oligomers, comprising the steps of:  
3 (a) providing a composition comprising at least two species of  
4 macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers  
5 comprising a structural repeat unit of the formula



6  
7 wherein

8 A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene  
9 group, and

10 B is a divalent aromatic or alicyclic group; and

11 (b) changing the weight percentage of at least one species of said  
12 macrocyclic polyester oligomers in said composition.

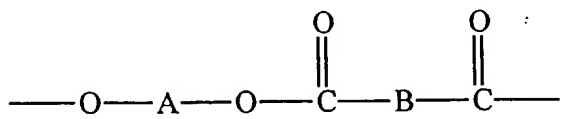
- 1 2. The process of claim 1 wherein said physical property is the melting  
2 temperature of said composition.

- 1 3. The process of claim 1 wherein said at least one species of said macrocyclic  
2 polyester oligomers in step (b) is the highest melting temperature macrocyclic  
3 polyester oligomer in said composition.

- 1 4. The process of claim 1 wherein said at least one species of said macrocyclic  
2 polyester oligomers in step (b) comprises at least said macrocyclic polyester  
3 tetramer.

- 1 5. The process of claim 4 wherein step (b) comprises reducing the weight  
2 percentage of at least the macrocyclic polyester tetramer.

- 1 6. The process of claim 1 wherein said at least two species of macrocyclic  
2 polyester oligomers in step (a) have a degree of polymerization from 2 to 10.
- 1 7. The process of claim 6 wherein said at least two species of macrocyclic  
2 polyester oligomers in step (a) have a degree of polymerization from 2 to 6.
- 1 8. The process of claim 1 wherein said composition comprises macrocyclic  
2 poly(1,4-butylene terephthalate) oligomers.
- 1 9. The process of claim 1 wherein said composition comprises macrocyclic  
2 poly(ethylene terephthalate) oligomers
- 1 10. The process of claim 1 wherein said composition comprises a macrocyclic  
2 copolyester oligomer
- 1 11. The process of claim 10 wherein said composition comprises a macrocyclic  
2 copolyester oligomer containing at least about 90 mole percent poly(1,4-  
3 butylene terephthalate) structural units.
- 1 12. The process of claim 1 wherein step (b) comprises performing fractional  
2 crystallization.
- 1 13. A macrocyclic polyester oligomer composition having a decreased melting  
2 temperature produced by the process of claim 1.
- 1 14. A macrocyclic polyester oligomer composition comprising at least two species  
2 of macrocyclic polyester oligomers, each of said macrocyclic polyester  
3 oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group,

and

B is a divalent aromatic or alicyclic group,

9 wherein a species of said macrocyclic polyester oligomers having the highest  
10 melting temperature is present in an amount less than or equal to 5%.

1 15. The composition of claim 14 wherein each of said macrocyclic polyester  
2 oligomers has a degree of polymerization in the range from 2 to about 6.

1 16. The composition of claim 15 wherein said species having the highest melting  
2 temperature is macrocyclic polyester tetramer.

1 17. The composition of claim 14 wherein said macrocyclic polyester oligomers  
2 comprise macrocyclic poly(1,4-butylene terephthalate) oligomers.

1 18. The composition of claim 14 wherein said macrocyclic polyester oligomers  
2 comprise macrocyclic poly(ethylene terephthalate) oligomers.

1 19. The composition of claim 15 wherein said macrocyclic polyester oligomers  
2 comprise a macrocyclic copolyester oligomer comprising at least about 90  
3 mole percent poly(1,4-butylene terephthalate) structural units.

1 20. The composition of claim 14 further comprising a filler.

1 21. The composition of claim 14 further comprising a polymerization catalyst.

1 22. A prepreg composition comprising the composition of claim 14.

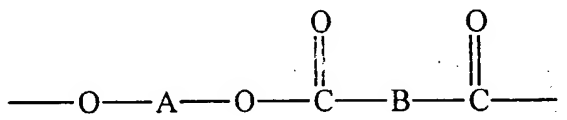
1 23. A blend material comprising:  
2 (a) the macrocyclic polyester oligomer composition of  
3 claim 14; and  
4 (b) a polymerization catalyst.

1 24. The blend material of claim 23 further comprising a filler.

1 25. The blend material of claim 24 wherein said filler is present at a weight  
2 percentage of from 0.1% to 70%.

1 26. A polyester polymer composite prepared by polymerizing said  
2 macrocyclic polyester oligomers of said blend material of claim 23.

- 1 27. An article of manufacture comprising said polyester polymer  
2 composite of claim 26.
- 1 28. A process for polymerizing a macrocyclic polyester oligomer  
2 composition comprising the steps of:  
3 (a) providing the macrocyclic polyester oligomer composition of claim  
4 14;  
5 (b) providing a polymerization catalyst; and  
6 (c) polymerizing said macrocyclic polyester oligomers.
- 1 29. A process for polymerizing a macrocyclic polyester oligomer  
2 composition comprising the steps of:  
3 (a) providing the blend material of claim 23; and  
4 (b) polymerizing said macrocyclic polyester oligomers.
- 1 30. The process of claim 29 wherein step (b) is conducted at a temperature  
2 between 130°C and 230°C.
- 1 31. A macrocyclic polyester oligomer composition comprising 30-40%  
2 macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5%  
3 macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers,  
4 each of said macrocyclic polyester oligomers comprising a structural repeat  
5 unit of the formula



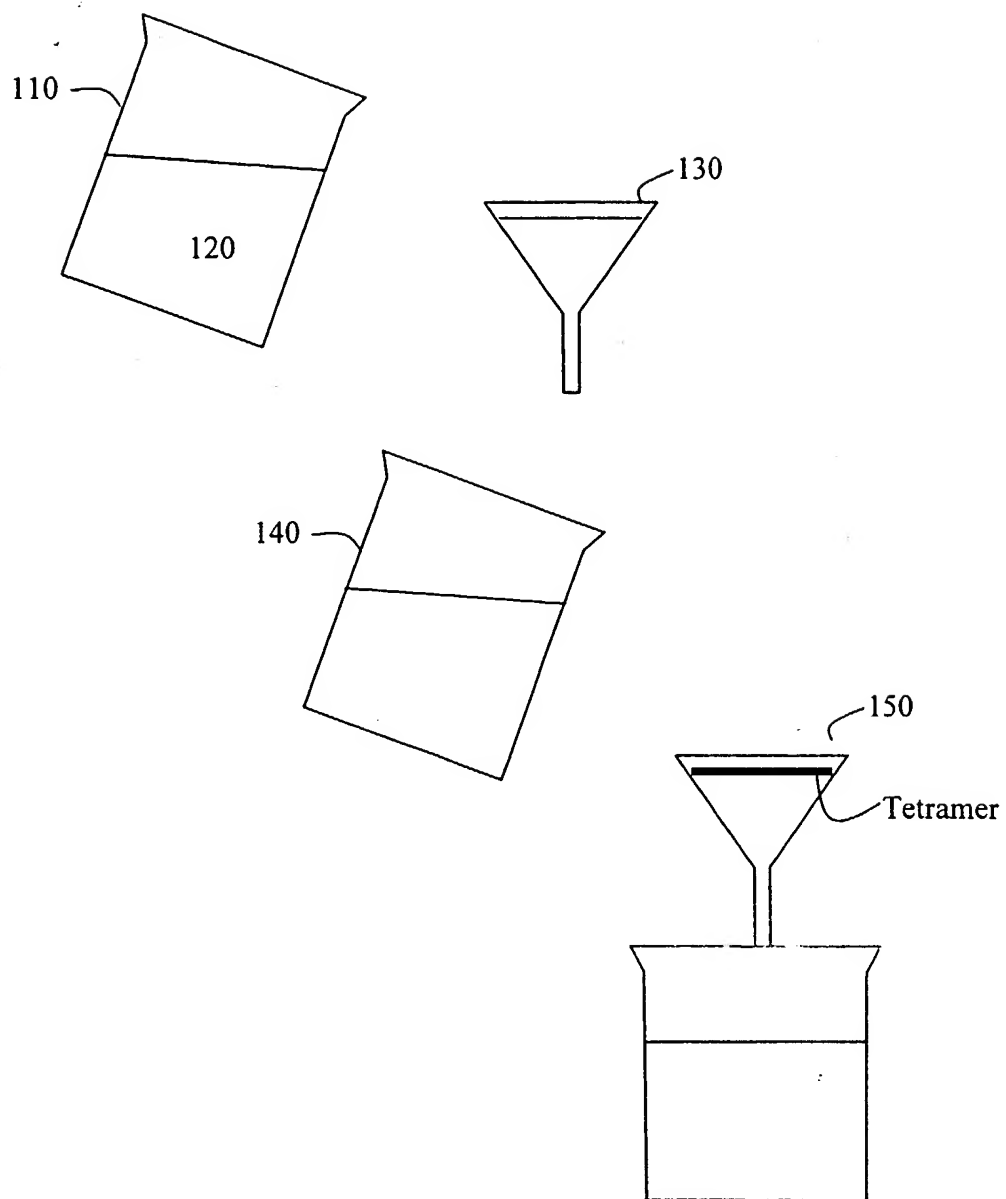
- 6  
7 wherein  
8 A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group,  
9 and  
10 B is a divalent aromatic or alicyclic group.
- 1 32. The composition of claim 31 wherein said macrocyclic polyester oligomer  
2 composition comprises less than 3% of macrocyclic polyester tetramers.

SPECIES MODIFICATION IN MACROCYCLIC POLYESTER  
OLIGOMERS, AND COMPOSITIONS PREPARED THEREBY

ABSTRACT

Physical properties, such as melting temperature of MPO compositions may be  
5 significantly modified by modifying the weight percentage of one or more of the constituent  
MPOs. For example, removal of a significant portion of the tetramer can afford low melting  
MPO compositions. In one aspect, the invention is related to a method for modifying a  
physical property of a MPO composition that includes the steps of (a) providing a  
composition that has at least two species of MPOs, and (b) changing the weight percentage of  
10 at least one species of the MPOs in the composition. In another aspect, the invention is  
related to a MPO composition that includes at least two species of MPOs where a species of  
the MPOs having the highest melting temperature is present in an amount less than or equal  
to 5%. In yet another aspect, the invention is related to a MPO composition comprising 30-  
40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic  
15 polyester tetramers, and 5-20% macrocyclic polyester pentamers.

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**Fig. 1**